REMARKS/ARGUMENTS

In view of the foregoing amendment, following remarks and the accompanying articles, reconsideration of the patentability of the pending claims is respectfully requested. Claim 35 has been amended to recite that the pulp being bleached has been pre-hydrolyzed. The subject matter of this amendment has previously been considered by the Examiner with respect to Claims 1 and 26, and therefore raises no new issues for the Examiner to consider.

Claims 1 and 2 stand rejected under 35 U.S.C. § 102 as being anticipated by U.S. Patent No. 6,512,110 to Heikkila. Claims 3 – 48 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Heikkila.

Independent Claim 1 recites the step of providing a pre-hydrolyzed cellulose pulp that is at least partially bleached. Independent Claim 26 recites a supply of an at least partially bleached pre-hydrolyzed cellulose pulp. Independent Claim 35 has been amended to now recite that the bleaching step comprises bleaching a pre-hydrolyzed cellulose pulp. Thus, independent claims 1, 26, and 35 recite a bleached pre-hydrolyzed cellulose pulp, or the step of bleaching a pre-hydrolyzed pulp. Independent Claim 48 recites providing a cellulose pulp that is at least partially bleached. As discussed below, Heikkila fails to disclose or suggest bleaching a pre-hydrolyzed pulp, or providing a cellulose pulp that is at least partially bleached.

The Examiner alleges that Heikkila teaches the step of bleaching a pre-hydrolyzed cellulose pulp. The Examiner's arguments are technically wrong for several reasons, and as will be discussed in greater detail below, Heikkila does not teach the step of bleaching a pulp, or that the pulp is pre-hydrolyzed prior to being bleached.

A.   Hiekkila does not teach the step of bleaching.

The Examiner alleges that xylanase treatment is a bleaching agent for pulp. The Examiner is mistaken. In support of his allegation, the Examiner has cited WO 9714803 to Breton et al. Specifically, the Examiner has offered the following quote from pages 9 and 10 of Breton in which Breton states "the use of xylanase as an auxiliary in the bleaching of paper pulp is all the more advantageous for the fact that the preparations are devoid of cellulose contaminants." (Emphasis mine). The key point in this excerpt is that xylanase is described as an auxiliary in the bleaching of paper and not as the bleaching agent itself. Merriam-Webster

Online Dictionary defines the term "auxiliary" to mean "**1 a :** offering or providing help **b :** functioning in a subsidiary capacity". Thus, as an auxiliary in the bleaching process, xylanase provides assistance, but is not actually the bleaching agent. As discussed below, it is common knowledge in paper pulping industry that xylanase is not capable of bleaching pulp in the absence of a bleaching agent.

It is well known that xylanase is not a bleaching agent and is in capable of bleaching pulp in the absence of a bleaching agent. Three articles have been attached to provide evidence that xylanase is not a bleaching agent, and to help more clearly explain the role of xylanase in the bleaching process. The first article, Pedersen et al., *Bleach Boosting of Kraft Pulp Using Alkaline Hemiceullulases*, Bleaching A Tappi Press Anthology, pgs. 289 - 303 (1993) (hereinafter "Pedersen"), describes the use of enzymes such as xylanase as a bleach booster that can be used to reduce the amount of chlorine needed in the conventional bleaching process. See page 290. Pedersen specifically states that the "enzyme stage cannot be considered a traditional bleaching stage as <u>it does not show any bleaching effect in itself.</u>" Id. at 291 (emphasis mine). The second article, Tolan et al., *The Use of Enzymes to Decrease the Cl_2 Requirements in Pulp Bleaching*, Bleaching A Tappi Press Anthology, pgs. 280 - 283 (1993), (hereinafter "Tolan"), states "[x]ylanase enzymes have been widely reported <u>to improve the effectiveness of conventional bleaching</u> chemicals in removing lignin from hardwood and softwood craft pulp." See page 280 (emphasis mine). Tolan further states that the "major effects of xylanase treatment are <u>only apparent after subsequent bleaching</u>" and that "xylanase acts to <u>enhance bleaching</u> by a different mechanism than does oxygen, chlorine, chlorine dioxide, and other chemical methods." Id. at 282 (emphasis mine). The last article, Li et al., *Bleachibility Improvements of Kraft Pulp by Alkaline Leaching and Xylanase Treatment*, Journal of Pulp and Paper Science, Vol. 22, pgs. 209 - 212 (June 1996) (hereinafter "Li'), explains how xylanase can be used to improve the bleachibility of pulp. Specifically, Li states that "the ability of xylanase enzyme to improve the bleachibility of pulps during subsequent chemical bleaching was first reported in 1986...." Id. at 207.

The above articles clearly establish that xylanase treatment does not bleach the pulp. Rather, the articles discuss and provide evidence that the xylanase treatment works in

conjunction with a conventional or subsequent bleaching process to help enhance bleaching of the pulp. This conclusion is further supported by the excerpt cited by the Examiner in Breton which refers to the use of xylanase as an "auxiliary". As noted above, the term auxiliary is defined as "offering or providing help" or "functioning in a subsidiary capacity", which is consistent with the use of xylanase in the above discussed articles. Thus, the attached articles including Breton show that xylanase does not bleach the pulp.

Since xylanase treatment cannot result in bleaching the pulp, the xylanase treatment described in Heikkila similarly cannot bleach the pulp. Thus, Heikkila fails to disclose or suggest the step of providing an at least partially bleached pulp as recited in independent Claims 1, 35, and 48, or a source of an at least partially bleached pulp as recited in Claim 26. Since Heikkila fails to disclose or suggest each and every step of Claims 1, 26, 35, and 48, these claims and any claims dependent thereon are patentable over the cited reference and it is respectfully submitted that the rejections under 35 U.S.C. § 102 and 103 have been overcome.

B. Heikkila does not disclose a pre-hydrolyzed pulp.

Heikkila fails to disclose or suggest the step of providing a pre-hydrolyzed pulp, or a source of a pre-hydrolyzed pulp. The Examiner alleges that Heikkila teaches the "treatment of the pulp with an aqueous solution of an alkali before the xylanase treatment." It is the Examiner's contention that the pre-treatment of the pulp with an aqueous solution of an alkali qualifies as pre-hydrolysis of the pulp. Specifically, the Examiner quotes the following excerpt from Heikkila: "in the alkali treatments optionally included in the process of the present invention, the solid pulp material to be treated is contacted or digested with an aqueous sodium hydroxide solution at a temperature of about 50 to 100° C." See page 4 of the final Office Action (quoting Heikkila column 6, lines 28 – 31). Hiekkila further elaborates on column 6, lines 37 – 40 that in the alkali treatment the "concentration of the sodium hydroxide in the aqueous sodium hydroxide solution is normally about 8 to 12 weight percent...."

Contrary to the Examiner's assertions, the alkali treatment described in Hiekkila is not a pre-hydrolysis treatment. In the kraft pulping industry, pre-hydrolysis has a specific meaning which refers to the pretreatment of the pulp under elevated temperature (e.g., 150 to 180° C) and

in an acidic environment. To help explain the meaning of term "pre-hydrolyzed", Applicants have provided an explanation of the term from Ingruber et al, Editor, Vol. 4 Sulfite Science & Technology, Pulp and Paper Manufacture, 3d ed., pg. 233 (hereinafter "Ingruber"). Ingruber describes prehydrolysis as an acidic pretreatment. Ingruber states that "[t]he prehydrolysis stage normally involves treatment of wood at elevated temperature (150 – 180° C) with dilute mineral acid (sulfuric or aqueous sulfur dioxide)...." Id. From Ingruber, it can be clearly seen that the term pre-hydrolyzed refers to a specific process in which the wood is treated in acidic conditions at elevated temperatures (e.g., 150 – 180° C). This is completely different than the alkali process described in Heikkila, which uses a basic solution (i.e., sodium hydroxide) at temperatures that are well below the temperatures used in preparing a pre-hydrolyzed pulp. Based on this understanding, it is clear that the alkali process described in Heikkila cannot be considered a prehydrolyis stage, and a pulp derived therefrom cannot be considered a pre-hydrolyzed cellulose pulp. Thus, Heikkila fails to disclose or suggest the step of providing a pre-hydrolyzed pulp, or a source of a pre-hydrolyzed pulp. Since, Heikkila fails to disclose or suggest a pre-hydrolyzed pulp, Claims 1, 26, and 35, and any claims dependent thereon are patentable over the cited reference.

In view of the foregoing amendment and remarks it is respectfully submitted that the rejections under 35 U.S.C. § 102 and 103 have been overcome, and that the pending claims are in condition for immediate allowance.

Conclusion

It is not believed that extensions of time or fees for net addition of claims are required, beyond those that may otherwise be provided for in documents accompanying this paper. However, in the event that additional extensions of time are necessary to allow consideration of this paper, such extensions are hereby petitioned under 37 CFR § 1.136(a), and any fee required

therefore (including fees for net addition of claims) is hereby authorized to be charged to Deposit Account No. 16-0605.

Respectfully submitted,

Timothy J. Balts
Registration No. 51,429

Customer No. 00826
ALSTON & BIRD LLP
Bank of America Plaza
101 South Tryon Street, Suite 4000
Charlotte, NC 28280-4000
Tel Charlotte Office (704) 444-1000
Fax Charlotte Office (704) 444-1111
LEGAL02/30067612v1

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BLEACHING

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BLEACH BOOSTING OF KRAFT PULP USING ALKALINE HEMICELLULASES

Lars Saaby Pedersen
Anne Mette Nissen
Novo Nordisk A/S
Novo Allé
DK-2880 Bagsværd
Denmark

Dana D. Elm
Paul P. Choma
Novo Nordisk Bioindustrials Inc.
33 Turner Road
Danbury
Connecticut 06813-1907
USA

ABSTRACT

Two alkaline xylanase preparations completely free of cellulase activity were tested for their ability to enhance the bleaching of softwood kraft pulp without causing any adverse effects on the strength properties.

Both enzymes show good bleach boosting effects at pH 8 and 9, respectively, without negatively affecting the strength properties of the pulp. Reduction in kappa number of up to 19% is obtained for an enzyme treated pulp compared to a control after a (D50 C50) E bleaching.

KEYWORDS

Enzymes, Xylanases, Bleaching, Kraft Pulp

INTRODUCTION

The kraft pulping process is the most common method used to produce a strong and bright pulp for high quality paper products.

An unbleached kraft pulp typically contains 3 to 5 percent residual lignin, which is removed in a multistage bleaching process involving oxidation and extraction stages. Normally one or more of the oxidative stages use chlorine or chlorine containing compounds as the oxidizing agent. The effluent from such bleaching plants is of growing environmental concern due to their content of numerous chlorinated organic substances, including chlorinated phenols and dioxins.[McKague, Jarl, Kringstad,1989]. There is great interest in

reducing the use of active chlorine in general, and Cl_2 in particular as this will reduce the pollution load of the effluent measured as AOX including chlorinated dioxins and dibenzofurans [Axegård, Renberg, 1989], which are of great concern.

One of the emerging technologies for reducing the amount of chlorine used in the bleaching of kraft pulp is the use of enzymes as a bleach booster. By treating a brown stock pulp with a xylanase, prior to the conventional bleaching sequence, the use of active chlorine in the subsequent bleaching stages can be reduced.

This concept of using a hemicellulase to improve the bleachability of a kraft pulp was originally presented in 1986 by [Viikari et al.,1986]. Since then a number of articles and papers have been published on this subject, eg. [Viikari et al., 1987], [Kantelinen et al., 1988], [Jurasek, Paice, 1988], [Paice, Bernier, Jurasek, 1988] and [Clark et al., 1989]. These papers show that the active chlorine dosage for bleaching a kraft pulp to a given kappa number after a (DC)E bleaching can be reduced by 15 to 25% dependent on the wood source and the enzyme used. All enzyme treatments are carried out at temperatures between 40 and 50°C, at pH between 4 and 5, pulp consistency 2.5 - 5% and treatment times of 12 to 24 hours.

The exact mechanism of the enzyme action on the pulp is not fully understood. Structural studies of the lignin hemicellulose matrix [Fengel, Wegener, 1989] show that the lignin and side groups on the polyoses are linked together in a three dimensional matrix by a number of ether and ester bonds. A possible explanation may be that the enzyme partially hydrolyses the xylan polymer releasing lignin fragments with short hemicellulose chains attached to it. The partial hydrolysis also allows for increased swelling of the pulp which facilitates the removal of the chlorinated/oxidized lignin fragments in the alkaline extraction stage.

Recent literature suggests [Puls et al., 1990] that xylanases, due to their molecular size, are not able to penetrate into the pulp fibers and therefore only act on the xylan at the surface of the pulp. This corresponds to the observation [Viikari, 1990] that the degree of bleach boosting effect by

xylanases correlates to the amount of reprecipitated xylan on the surface of the fibers.

The enzyme stage can not be considered a traditional bleaching stage as it does not show any bleaching effect in itself. It improves the performance of the subsequent bleaching stages or boosts the bleaching.

For industrial scale application the most relevant site to introduce the enzyme stage is prior to the first chlorine containing bleaching stage in order to reduce the amounts of effluent from this stage.
In a kraft mill the pulp is normally at alkaline pH, and residence times of more than 2 to 4 hours are normally not available in between the digester and the bleaching plant .

None of the bleach boosting applications of hemicellulases described in the literature deals with hemicellulases that meet these conditional requirements. All the enzymes mentioned are working at acid pH (4 to 5) and seem to require long treatment times (12 to 24 hours).

The aim of the work presented below is to demonstrate that alkaline xylanses completely free of cellulase side activity are able to boost the bleachability of softwood kraft pulp under conditions as close as possible to mill conditions.
The paper is based on results obtained with two different alkaline xylanase preparations.

MATERIALS

Enzymes:
Two cellulase free, alkaline xylanase preparations have been tested. The two preparations named SP473 and SP406 are xylanases of bacterial and fungal origin, respectively.

Pulp:

All the work on SP473 and the dosage, pH and temperature response experiments on SP406 have been carried out on O_2 delignified Swedish pine kraft pulp. Initial kappa number: 16.7.

The last set of experiments with SP406 was made on mixed North American softwoods, Initial kappa number: 26.2.

METHODS

Enzyme assay:

The enzyme activity is measured as Endo Xylanase Units (EXU-units). The method is based on colour release from blue dyed xylan [Biely et al.,1985].

The enzyme is incubated for 30 minutes with Remazol Brilliant Blue dyed xylan at pH 9.0 and 50°C. Afterwards the non degraded substrate is precipitated with ethanol. The blue colour of the supernatant is measured at 585 nm and the activity is determined relative to the colour release obtained by an enzyme standard [Novo Nordisk A/S, Analytical Method,1990].

Monosaccharide analysis:

The liquid phase obtained from the enzyme treatment stage is filtered through a 0.45 μm filter. The filtrate is freeze-dried and hydrolyzed for two hrs using 2 N Trifluoroacetic acid (TFA) at 100°C. The TFA is then removed by evaporation and the sample is redissolved in demineralized water. The monosaccharide composition of the hydrolyzed sample is determined by Ion Exchange HPLC followed by electrochemical detection. [Hardy et. al., 1988]

Pulp and Paper Analysis:

The kappa number, viscosity, tear and tensile strengths, brightness and density are all determined according to the SCAN standards.

Enzyme Treatment:

The enzyme treatment of the pulps has been carried out at a temperature of 50°C and 10% consistency for 3 hours. The pH was controlled by using a Britton Robinson Buffer. The enzymes were dosed based on EXU-units. Control samples ("0 EXU/kg") were run in parallel with the samples receiving an enzyme treatment, but with addition of demineralized water instead of enzyme solution.

The pulp was washed with cold demineralized water after the enzyme treatment.

(DC)E bleaching sequence:
(DC)E bleaching trials have been carried out using 50 % substitution with chlorine dioxide at the following conditions:

		(D50 C50) Stage	E Stage
Temperature	:	40°C	60°C
Time	:	45 min	60 min
Consistency	:	5 %	10 %

The amount of NaOH applied in the E stage is adjusted according to the dosage of aCl in the (DC) stage.

(D50 C50)ED Bleaching sequence:
In order to determine the overall savings of active chlorine as well as effects on the strength properties the pulps were bleached to final brightness.

The experiments are made in the following way. The enzyme treated samples and the control are bleached to the same kappa number after (D50 C50)E by adjusting the aCl dosage in the (D50 C50) stage. (D50 C50) E bleaching conditions as listed above.

The conditions used in the D stage were 70°C for 3 hrs at 10% consistency, and pulps were bleached to the same final brightness.

RESULTS AND DISCUSSION

SP473

Dosage response trials were performed with an enzyme stage followed by a (D50 C50)E bleaching sequence. The enzyme treatment was performed at pH 8.0, 9.0 or 10.0.

In Table 1 the results at pH 8.0 are shown. A good enzyme effect is observed. At pH 9.0 only half the effect is seen and at pH 10.0 no effect is observed. (data not shown).

TABLE 1. Results from Sp473 dosage response trial at pH 8.0 and 50°C.

ENZYME DOSAGE (EXU/kg)	AFTER ENZYME		AFTER (D50 C50)E	
	x-no	x-no reduction	x-no	x-no reduction
0	14.95	Basis	4.22	Basis
50	14.60	2 %	3.81	10 %
124	14.43	3 %	nd	nd
247	14.22	5 %	3.55	16 %
743	14.11	6 %	3.44	19 %

nd : Not determined

In the (D50 C50) stage all pulps are bleached using the same dosage of active chlorine, namely 0.2 times the kappa number of the control (0.2*14.95 = 2.99 %)

The monosaccharide composition of acid hydrolysed samples of water pressed out of the pulp after the enzyme stage are given in Figure 1.
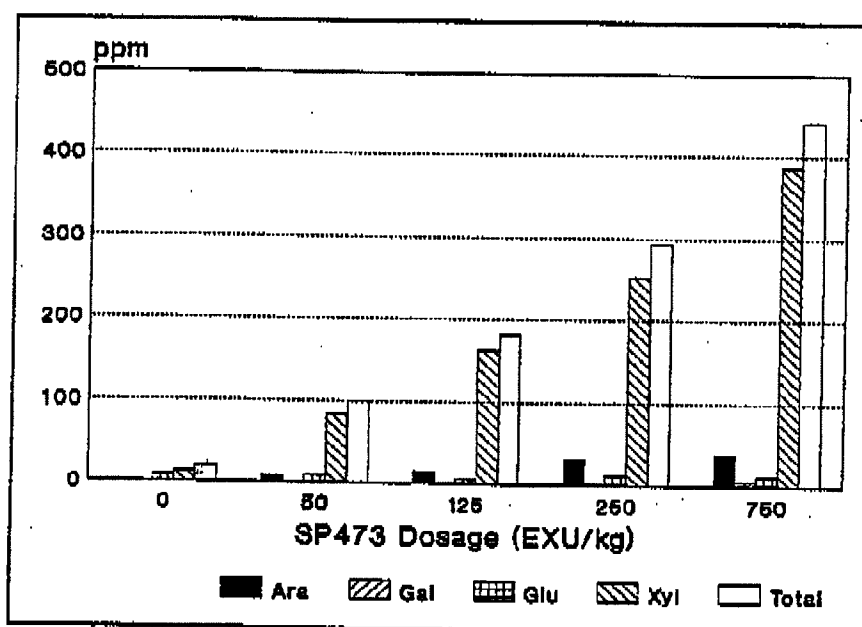

Figure 1. Monosaccharide Composition of acid hydrolysed samples of the filtrate after the Enzyme Stage.

From Figure 1 it is clearly seen that SP473 is a xylanase without any significant cellulase activity. The xylose content of the sample accounts for 85-90 % of the total

monosaccharides present, whereas glucose is hardly detec-
table.

The hemicellulose component of softwood expected to be in
largest quantity at this stage in the process is arabino(4-O-
methyl-glucorono)xylan with a proportional relationship
between xylose and arabinose of around 10:1.3. [Eriksson, K.-
E.L., R.A. Blanchette, R.A. and Ander, P., 1990].
The data in figure 1 shows a xylose-arabinose ratio of about
10:1.

To compare the monosaccharide analysis with bleaching
results, the kappa number after (D50 C50) E and the xylose
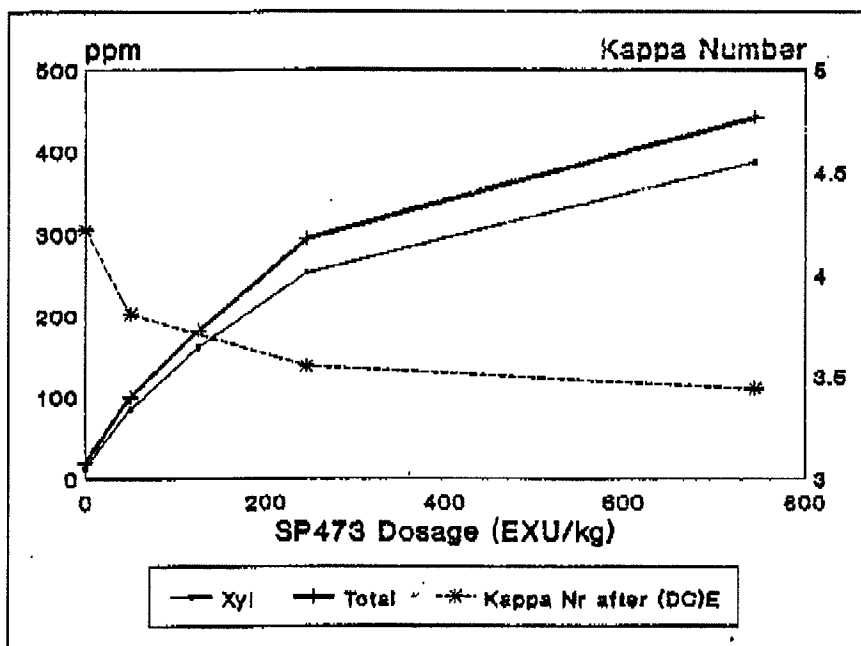and total monosaccharide content were plotted versus enzyme
dosage (Figure 2).

Figure 2. Comparison of Kappa Number after (DC)E
stage with the xylose and total monosaccharide
content of acid hydrolysed samples of the filtra-
tes after the enzyme stage.

The kappa number reduction versus enzyme dose is mirrored
concomitant to an increased release of monosaccharides.

Optimum temperature and pH conditions for enzyme efficacy
were determined by measuring the release of monosaccharides.
The effect of pH and temperature are given in figures 3 and
4, respectively.

The data show the optimum pH and temperature is 8 and 50°C,
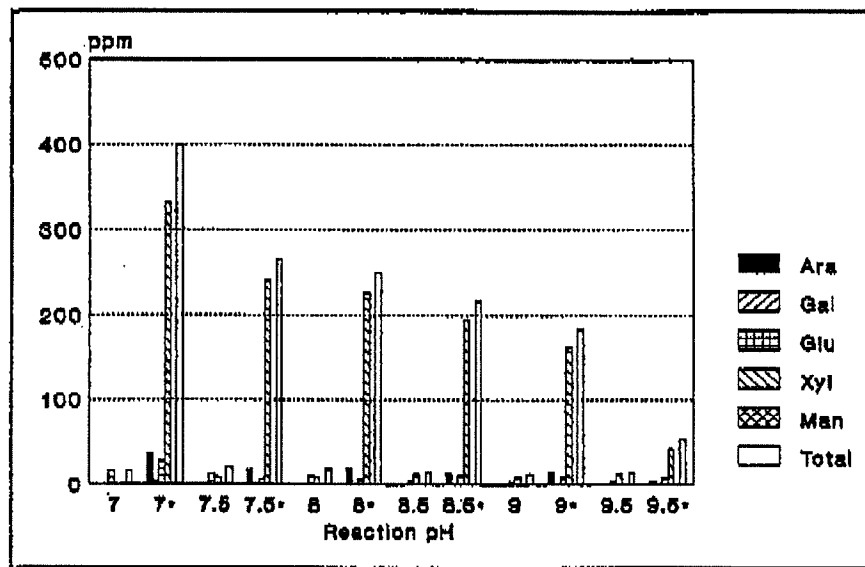respectively.

Figure 3. Monosaccharide content of acid hydroly-
sed samples of the filtrate after enzyme treat-
ment at 50°C and various pH values. The * desig-
nates SP473 treated (515 EXU/kg), whereas the un-
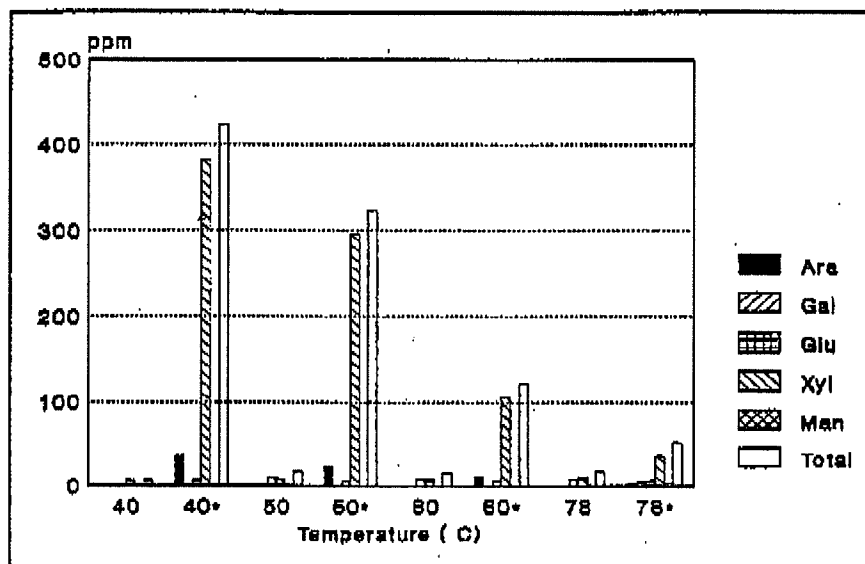marked figures are controls.

Figure 4. Monosaccharide content of acid hydroly-
sed samples of the filtrate after enzyme treat-
ment at pH 8.0 and various temperatures. The *
designates SP473 treated (515 EXU/kg), whereas
the un-marked figures are controls.

A (D50 C59)E bleaching sequence was performed on pulps treated with SP473 dosages of 0 (= control) and 575 EXU/kg dry pulp. The bleaching results are listed in Table 2 below.

TABLE 2. Data concerning the (D50 C50)E stage.

	CONTROL	SP473
κ-no after enzyme stage	15.85	15.02
aCl dosage in (D50 C50)	3.48 %	3.15 %
κ-no after (D05 C50)E	2.93	2.62

It is seen, that at least a 9.5 % saving in aCl dosage in the (D50 C50) stage can be obtained.

After the final D stage, where the pulps were bleached to 90 %(ISO) brightness, viscosity as well as strength properties were determined. Table 3 shows the intrinsic viscosity $[\eta]$ and DP [calculated according to Evans, R., Wallis, A.F.A., 1987]. The results from strength properties testing are given in figure 5. From these results it is seen that SP473 does not adversely affect the strength properties of the pulp.

Finally, treatment with SP473 resulted in an overall yield loss of only 0.5% relative to the control.

Table 3 Viscosity of the pulps.

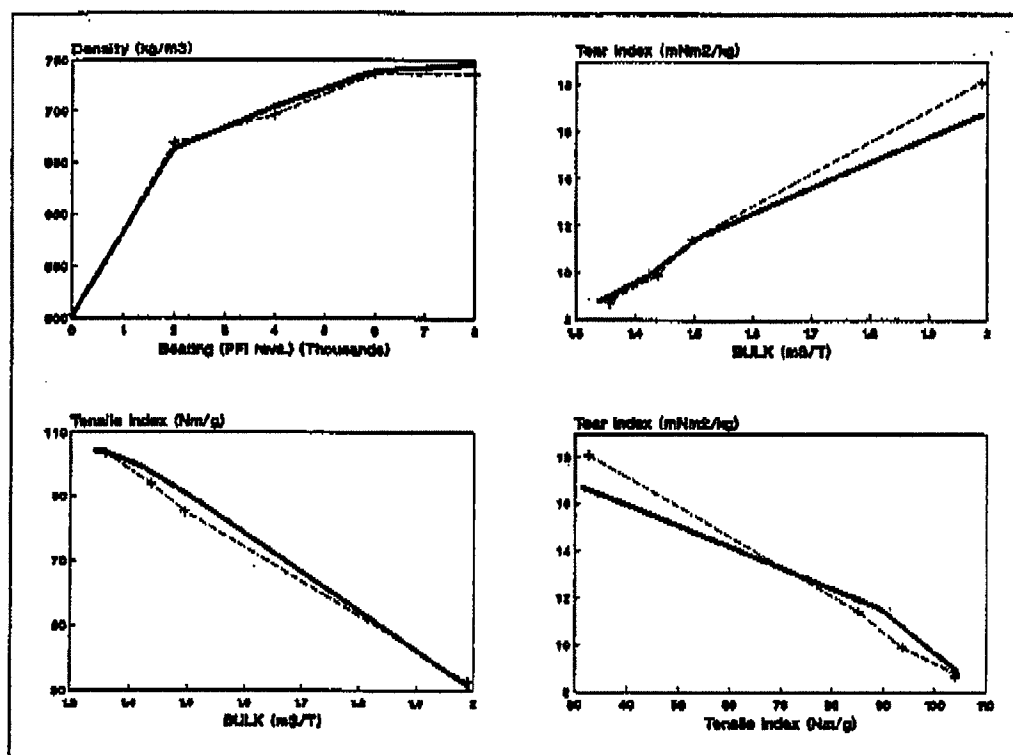|	CONTROL	SP473
$[\eta]$ (dm^3/kg)	869	863
DP	3210	3185

Figure 5. Comparison of selected handsheet properties for control (———) and SP473 (-x- -) treated Swedish O$_2$ delignified kraft pine pulps.

SP406

Dosage response trials for this enzyme were made in the same way as previously shown for SP473. The enzyme treatment was performed at pH 8.0, 9.0 or 10.0, respectively and followed by a (D50 C50) E stage bleaching. The enzyme is performing well at both pH 8.0 and 9.0. At pH 10.0 a slight enzyme effect is seen. The results obtained at pH 9.0 are shown in table 4.

TABLE 4. Results from SP406 dosage response trial
at pH 9.0 and 50°C.

ENZYME DOSAGE (EXU/kg)	AFTER ENZYME		AFTER (D50 C50)E	
	x-no	x-no reduction	x-no	x-no reduction
0	14.45	Basis	3.43	Basis
150	13.80	4.5 %	2.98	13 %
250	13.62	5.7 %	2.83	17 %
500	13.40	7.3 %	2.71	21 %
1000	13.15	9.0 %	2.74	20 %

Temperature and pH Curves based on monosaccharide analysis of water pressed out of the enzyme treated pulp are given in the figures 6-7.

From the Figures it is seen that SP406 is a cellulase free xylanase. The enzyme shows good performance at temperatures up to 50°C and pH up to 9.0.
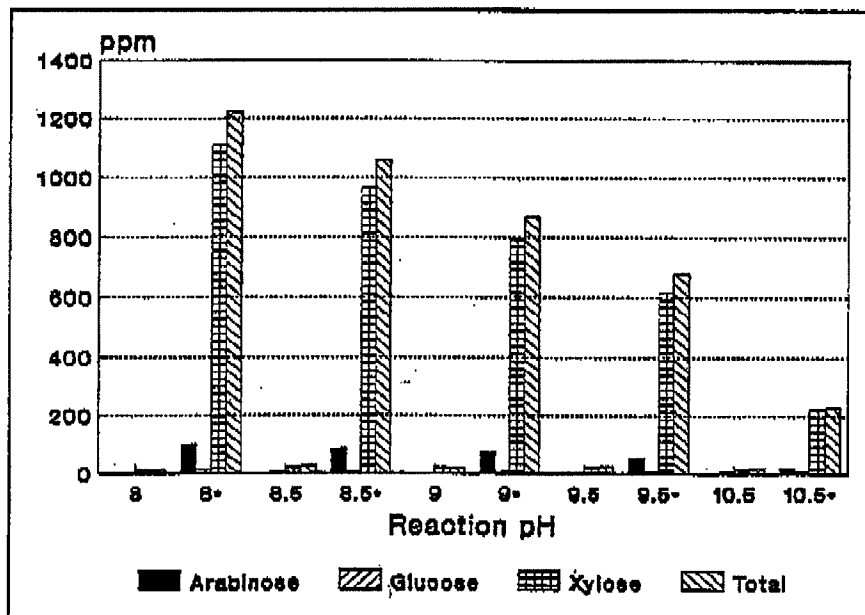

Figure 6. Monosaccharide content of acid hydroly-
sed samples of the filtrate after enzyme treat-
ment at 50°C and various pH values. The * desig-
nates SP406 treated (1000 EXU/kg) samples,
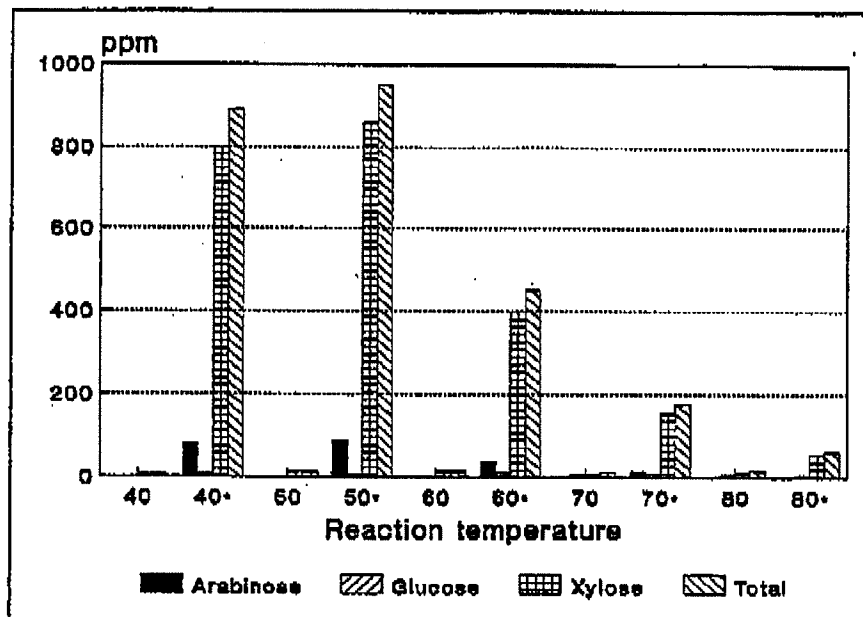whereas the un-marked figures are controls.

Figure 7. Monosaccharide content of acid hydolysed samples of the filtrate after enzyme treatment at pH 8.0 and various temps. The * designates the SP406 treated (1000 EXU/kg) samples, whereas the un-marked figures are controls.

Bleaching to 85 %ISO brightness was performed on North American softwood pulp. The bleach boosting stage was performed at pH 9.0, 50°C and 10% consistency for 3 hours and dosages of SP406 corresponding to 0 (control) and 1250 EXU/kg dry pulp, respectively. Results are given below.

TABLE 5. Data concerning the (D50 C50)E stage.

	CONTROL	SP406
κ-no after enzyme stage	25.54	25.40
aCl dosage in (D50 C50)	5.56 %	4.82 %
κ-no after (D50 C50)E	5.04	5.24

It is seen, that a 13 % saving in aCl dosage was obtained.

After the final D stage, where the pulp is bleached to 85 %ISO brightness, the strength properties were tested. The results are given in Figure 8 below.
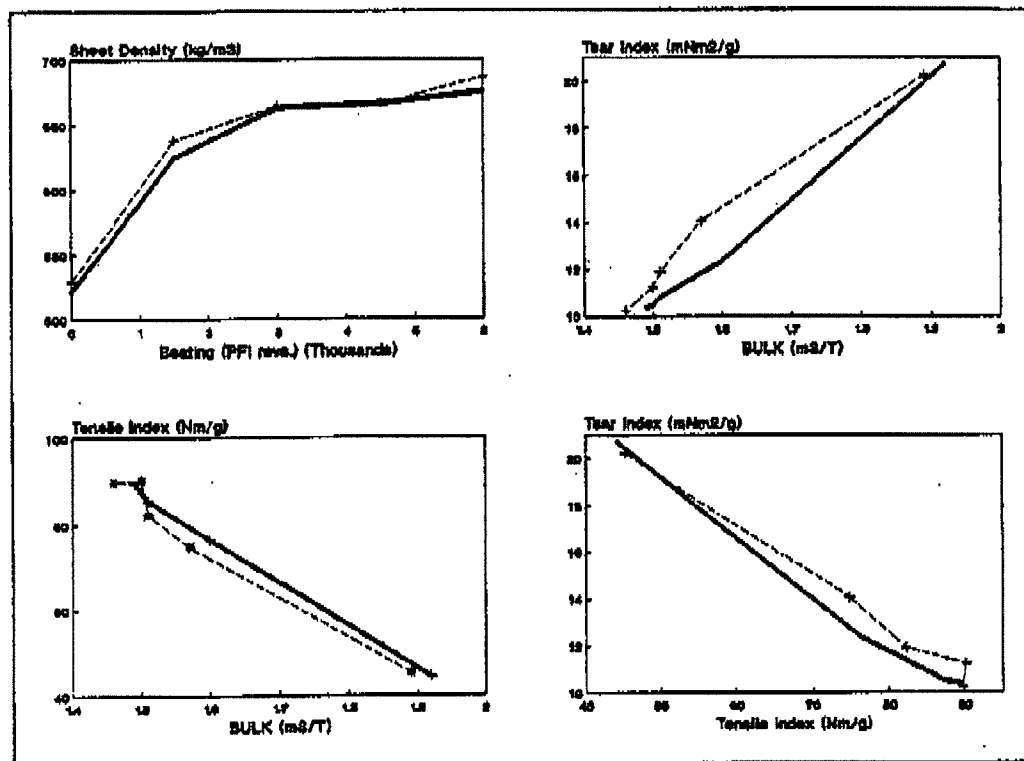
Figure 8. Comparison of selected handsheet properties for control (———) and SP406 (-x- -) treated North American mixed softwood kraft pulp.

The SP406 treatment does not give any adverse effects on the strength properties of the pulp.

CONCLUSION

The aim of the reported work is to show that alkaline xylanase preparations completely free of cellulase activity are able to boost the bleachability of kraft pulp without negatively affecting the strength properties.

This is demonstrated for two different alkaline xylanase preparations.

From our previous work made with other xylanases it is known that the benefit of an enzyme bleach boosting stage can be taken to shift the degree of substitution in the first bleaching stage towards higher chlorine dioxide levels while maintaining the total dosage of active chlorine. The same is expected to be the case for these enzyme preparations.

The reduction in active chlorine obtained in this study is lower than previously reported in the literature. The reason is that the enzyme treatments were carried out on the edge of the working range of the enzymes with regard to pH and temperature. This was done in order to resemble mill conditions as closely as possible. If the enzyme treatment had been carried out at optimal conditions for the enzymes better performance would have been obtained.

The isolation of more alkaline and thermostable xylanases that even more closely match the conditions of the pulp after kraft cooking is predicted for the future.

REFERENCES

Axegård, P., Renberg, L., 1989: The influence of bleaching chemicals and lignin content on the formation of polychlorinated dioxins and dibenzofurans. Chemosphere, Vol.19, nos.1-6, pp 661-668, 1989

Biely, P., Mislovicova, D., Toman, R., 1985: Soluble chromogenic substrates for the assay of endo-1,4-beta-xylanases and endo-1,4-beta-glucanases (cellulases), Anal. Biochem. Vol. 144, 1, p 142-146, 1985.

Eriksson, K.-E.L., R.A. Blanchette, R.A. and Ander, P., 1990, "Microbial and Enzymatic Degradation of Wood and Wood Components", Springer Verlag Berlin, Heidelberg, Germany, 1990)

Evans, R., Wallis, A.F.A., (1987), Comparison of cellulose molecular weights determined by high performance size exclusion chromatography and viscometry. Fourth Int. Symp. Wood Chem., Paris, April, 1987, 201-205.

Fengel, D., Wegener, G., (1989), Wood Chemistry, Ultrastructure, Reactions, Walter de Gruyter, Berlin 1989

Hardy et. al., 1988, Analytical Biochemistry, 170, pp 54-62 (1988)

Jurasek, L., Paice, M.G. (1988) Biological Bleaching of Pulp, Proceedings. International Pulp Bleaching Conference, Orlando, June 5-9, p 11-13

Kantelinen, A., Rättö, M., Sundquist, J., Ranua, M., Viikari, L., Linko, M. (1988) Hemicellulases and their Potential Role in Bleaching, Proceedings. International Pulp Bleaching Conference, Orlando, June 5-9, p 1-9

McKague, A.B., Jarl, M., Kringstad, P., 1989: An up-to date list on components identified in bleachery effluents as of January 1989. SSVL Miljö 90: Subproject "Bleaching"

Novo Nordisk A/S, 1990, Analytical Method AF 293.9/1-GB, Endo-Xylanase determination, pH 9.0

Paice, M.G., Bernier, Jr., Jurasek, L., (1988) Viscosity-Enhancing Bleaching of Hardwood Kraft Pulp with Xylanase from a Cloned Gene. Biotech. bioeng., Vol. 32, pp. 235-239, 1988.

Puls, J., Poutanen, K., Lin,J.J., (1990) Accessibility of hemicellulose in hardwood pulps to enzymes, Biotechnology in Pulp and Paper Manufacture, Butterworth-Heinemann, 1990.

Viikari, L., Ranua, M., Kantelinen, A., Sundquist, J., Linko, M. (1986) Bleaching with Enzymes. The Third International Conference on Biotechnology in the Pulp and Paper Industry, Stockholm, 16-19.6.1986, p67-69

Viikari, L., Ranua, M., Kantelinen, A., Linko, M., Sundquist, J. (1987) Application of enzymes in bleaching. Proceedings. International Symposium on Wood and Pulping Chemistry, Paris, April 27-30, 1987, Vol. 1, p 151-154

Viikari, L., (1990), Biotechnical methods in pulp bleaching, oral presentation at Challenges and Possibilities for Biotechnology in the pulp and paper industry, October 17-18,1990, Hanaholmen, Helsingfors, Finland.

THE USE OF ENZYMES TO DECREASE THE Cl₂ REQUIREMENTS IN PULP BLEACHING

Xylanase enzymes improve effectiveness of conventional chemical bleaching

BY J.S. TOLAN AND R. VEGA CANOVAS

J.S. Tolan,
Iogen Corp.,
Ottawa, Ont.

R. Vega
Canovas, CPFP
Research Ltd.,
Hawkesbury,
Ont.

XYLANASE ENZYMES have been widely reported to improve the effectiveness of conventional bleaching chemicals in removing lignin from hardwood and softwood kraft pulp [1-4]. Xylanase enzymes partially hydrolyze the hemicellulose portion of pulp. These enzymes contain only minimal amounts of the activity for degrading the cellulose and lignin fractions of the pulp (i.e. cellulase and ligninase). Surprisingly, ligninases have not been effective in enhancing pulp bleaching [1]. Cellulases have not helped in the bleaching of pulp and have had a deleterious effect on pulp yield and quality.

Although the precise mechanism by which xylanase enhances pulp bleaching is not clear, it appears that a partial hydrolysis of xylan improves the susceptibility of lignin to removal by the subsequent chlorination and alkali extraction stages. Xylan constitutes over 90% of the hemicellulose in hardwood kraft pulp and 50% of that in softwood pulp.

Xylan certainly creates a physical barrier to chlorine and sodium hydroxide accessibility to the lignin. In addition, there is evidence that xylan and lignin are chemically bound [5]. It is possible that xylanase cuts these linkages, thereby enhancing lignin removal by both chlorination and alkali extraction.

In published laboratory studies, xylanase enzymes have been used to treat washed brownstock prior to bleaching. Typical conditions for xylanase treatment are 18 h at 50°C, pH 5. The enzyme treatment has been shown to increase the amount of lignin that can be extracted by alkali. After extraction, the kappa number of the enzyme-treated pulp is 2 to 4 units less than untreated pulp [1,3,4]. Paice, et al. [3] made handsheets from enzyme-treated pulp with no compromise in freeness, burst, tear, or tensile strengths.

Mill scale trials of xylanase treatment have been carried out successfully on softwood kraft pulp on a production scale [6]. Enzyme was used in an 800-tonne pulp run with the bleaching sequence (DC)EDED (80% substitution of chlorine dioxide for chlorine in delignification). Xylanase decreased the bleaching chemical requirements by 12% relative to untreated (DC)EDED pulp. The xylanase-treated pulp had equivalent tensile, burst, and tear strengths to the untreated pulp. These results indicate that xylanase treatment can be implemented on a large scale.
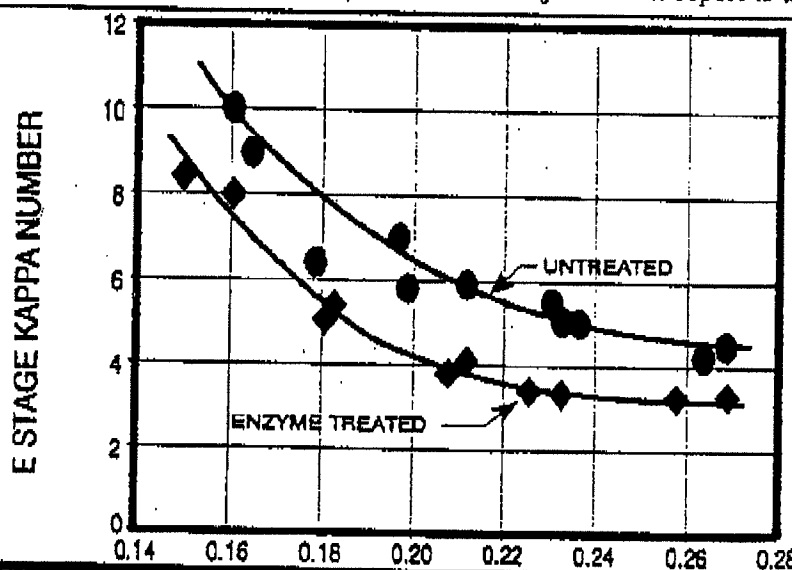
The subject of this report is the

FIG. 1. THE E-STAGE KAPPA NUMBER AS A FUNCTION OF THE KAPPA FACTOR FOR ENZYME-TREATED PULP AND UNTREATED PULP. THE ENZYME TREATMENT WAS WITH 2.5 L/T XYLANASE AT 50°C FOR 16 H. THE ENZYME GIVES A BENEFIT OF ABOUT 2 POINTS IN KAPPA NUMBER.

treatment of Canadian softwood kraft pulp with xylanase enzyme. We measured the benefits of enzyme treatment in the (CD)EDED bleaching sequence, to directly assess the performance of the enzyme in delignification and brightening. We also made a preliminary assessment of the benefits of enzyme treatment in bleaching sequences with high chlorine dioxide substitution.

EXPERIMENTAL WORK

Washed softwood kraft brownstock was obtained from an eastern Canadian mill.

Iogen xylanase enzyme was used for the enzyme treatments. It is a liquid solution containing active protein. Twelve to 17 grams of pulp (dry basis) was treated in plastic bags. The pulp was diluted with water to 10% solids consistency, then adjusted to pH 4.8 with a 10% sulphuric acid solution. The enzyme was added after pH adjustment and manually dispersed. The plastic bags were then placed in a 50°C water bath for periods of time ranging from 30 min, to 16 h. Untreated pulp was

brought through the same procedure, except that no enzyme was added.

Enzyme dosage is defined in millilitres of enzyme solution per tonne of dry pulp (mL/t). The enzyme solution has a xylanase activity of 2000 units/mL (based on hydrolysis of oat spelt xylan) and negligible cellulase activity.

In most experiments, the pulp (kappa number 27.8) was fully bleached to a target 90 brightness by a conventional (CD)EDED bleaching sequence, with 10% chlorine dioxide substitution in the chlorination stage. The (CD) stage was carried out at 2.5% consistency in
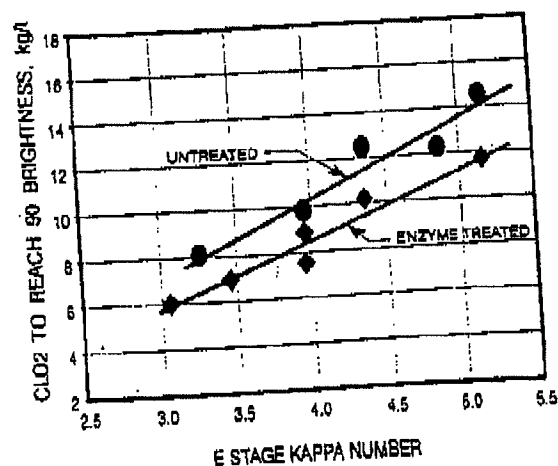

FIG. 2. THE CHLORINE DIOXIDE REQUIRED (D1 + D2) TO REACH 90 BRIGHTNESS FOR A GIVEN E-STAGE KAPPA NUMBER. THE DATA ARE FOR ENZYME-TREATED PULP (2.5 L/t FOR 16 H) AND UNTREATED PULP.

FIG. 3. EFFECT OF ENZYME TREATMENT TIME ON (CD)ED BRIGHTNESS XYLANASE TREATMENT WAS CARRIED-OUT WITH 500 ML/t ENZYME FOR VARIOUS TIMES FOLLOWED BY (CD)ED BLEACHING WITH KAPPA FACTOR 0.22 IN THE CHLORINATION STAGE AND 0.8% CHLORINE DIOXIDE ON PULP IN THE D STAGE. MOST OF THE BENEFIT OF A 16-H ENZYME TREATMENT CAN BE OBTAINED IN 1 H.
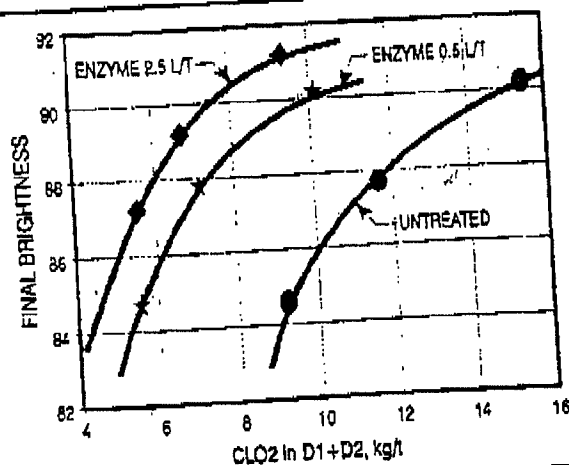

FIG. 4. THE EFFECT OF ENZYME TREATMENT ON THE BRIGHTNESS OF (CD)EDED BLEACHED PULP. PULP WAS TREATED WITH ENZYME AT DOSAGES OF 0 L, 0.5 L AND 2.5 L/t FOR 16 H. THE PULP WAS THEN BLEACHED WITH CHLORINATION KAPPA FACTOR 0.21 FOLLOWED BY EXTRACTION. THE BRIGHTNESS IS SHOWN AS A FUNCTION OF THE CHLORINE DIOXIDE CONSUMPTION IN THE DED BRIGHTENING STAGES.

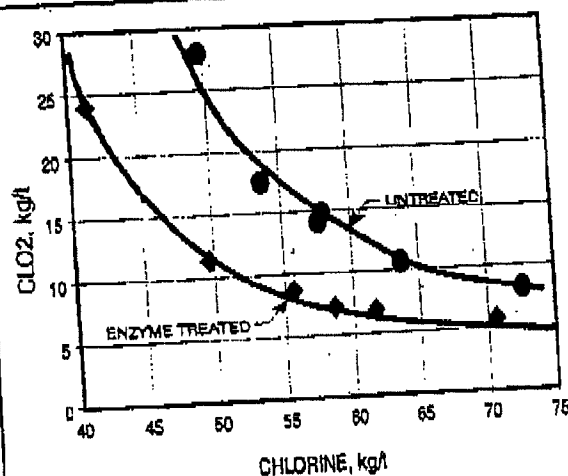FIG. 5. THE EFFECT OF XYLANASE ON CHLORINE AND CHLORINE DIOXIDE REQUIREMENTS TO REACH 90 BRIGHTNESS. PULP WAS SUBJECTED TO (CD)EDED BLEACHING WITH AND WITHOUT 2.5 L/t ENZYME TREATMENT FOR 16 H. THE COMBINATION OF CHLORINE AND CHLORINE DIOXIDE LEVELS NEEDED TO REACH 90 BRIGHTNESS ARE INDICATED.

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Mason jars.

Chlorine and chlorine dioxide were premixed and then added to the pulp. The temperature was maintained at 40°C in a water bath. The residual chlorine was measured at the end of the (CD) stage and was always less than 5% of the initial amounts. The E-stage kappa number and the brightness of the pulp after (CD)ED bleaching was also measured. Extraction stages were carried out at a caustic loading of 0.6 times the active chlorine in the chlorination stage. The pulp yield was not measured.

In some cases, 420 g (OD) pulp samples (kappa number 32.3) were treated in a stirred tank reactor. Following the enzyme treatment, the pulps were bleached either by the $(D_{45}, C_{50}+D_5)(E_O)DED$ or $D_{100}(E_O)DED$ bleaching sequences. For the $(D_{45}, C_{50}+D_5)$ stage, the time lag between initial chlorine dioxide charge and the addition of chlorine plus chlorine dioxide was two min. Standard (E_O)-stage treatments were carried out on these pulps.

RESULTS & DISCUSSION

Enzyme treatment: The major effects of xylanase treatment are only apparent after subsequent bleaching. The xylanase enzyme treatment, without further processing, has very little evident effect on the softwood pulp. Xylanase treated pulp, when washed with water, has an insignificant 0.5 unit decrease in kappa number relative to untreated pulp. The xylanase solubilizes 2% of the lignin in the brownstock, as indicated by absorbance measurement at 281nm, the wavelength associated with lignin's aromatic ring.

Delignification by (CD)E stages after enzyme treatment: Xylanase enzyme treatment leads to a decrease in the E-stage kappa number of about two units relative to untreated pulp, Fig. 1. This allows a 20% decrease in chlorine use to delignify pulp to kappa number 4 to 5. A 10% chlorine reduction is obtained at kappa number 6 to 8.

Pulps delignified to a given E-stage kappa number are also easier to brighten in subsequent (DED) stages if they have undergone xylanase treatment. When treated and untreated pulps of the same E-stage kappa number are compared, Fig. 2, treated pulps demonstrate a lower chemical requirement to reach the same brightness.

The results indicate that from a given E-stage kappa number, 15% less chlorine dioxide is required to reach a given brightness level for enzyme-treated pulp than for untreated pulp. Therefore, a xylanase treatment enhances the performance of conventional bleaching chemicals in both the brightening and delignification stages.

Xylanase's ability to improve both delignification and brightening is surprising in comparison to other bleaching chemicals. Chlorine dioxide substitution in the chlorination stage decreases the amount of active chlorine required to reach a given E-stage kappa number, but has no effect on subsequent brightening [7]. Oxygen delignification has a substantial effect on the delignification stages. Although there have been some reports of enhancement of the brightening stages [8,9] this point is not clear.

Xylanase enzyme acts to enhance bleaching by a different mechanism than does oxygen, chlorine, chlorine dioxide, and other chemical methods. Some lignin which may be particularly recalcitrant to removal by chemical treatment, because it is chemically bound to carbohydrates, might have its removal facilitated by xylanase's novel attack mechanism.

Enzyme treatment time: Xylanase treatment can give an 8 point brightness gain in a (CD)ED bleaching sequence, Fig. 3. Roughly two thirds of this brightness gain is achieved after only one hour of treatment. The fact that the brightness boost is insensitive to the treatment time shows that there is flexibility in the implementation of enzyme treatment in a mill.

Chemical savings from enzyme treatment: Xylanase's brightening capability can be used to decrease the ClO_2 requirement to reach 90 brightness by as much as 50%, Fig. 4, for a given kappa factor in the chlorination stage. Xylanase treatment is effectively a substitute for 5 kg/t of chlorine dioxide.

Testing similar to that shown in Fig. 4 was carried out at various chlorine loadings in the (CD) stage. The results are used to determine the combinations of chlorine and chlorine dioxide required in (CD)EDED bleaching to reach 90 brightness, as shown in Fig. 5. As one would expect, the chlorine dioxide requirement increased with decreasing chlorine use in the (CD) stage. As the chlorine is decreased to a low level, a critical chlorine level is reached, below which 90 brightness cannot be obtained. This minimum chlorine level is about 48 kg/t for untreated pulp and 39 kg/t with
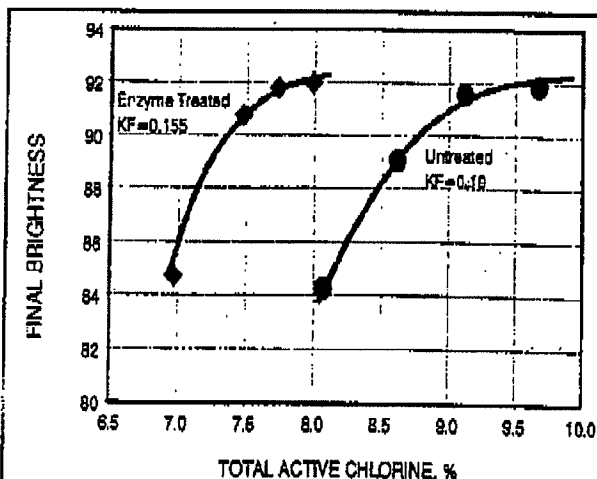
FIG. 6. THE EFFECT OF ENZYME TREATMENT ON CHLORINE REQUIREMENTS IN A (DC)(E₀)DED BLEACHING SEQUENCE WITH 50% CHLORINE DIOXIDE SUBSTITUTION IN THE CHLORINATION STAGE. THE GRAPH SHOWS THE BRIGHTNESS OF THE BLEACHED PULP AS A FUNCTION OF THE TOTAL ACTIVE CHLORINE CONSUMED. THE ENZYME TREATMENT WAS FOR 2 H WITH 500 ML ENZYME/t.
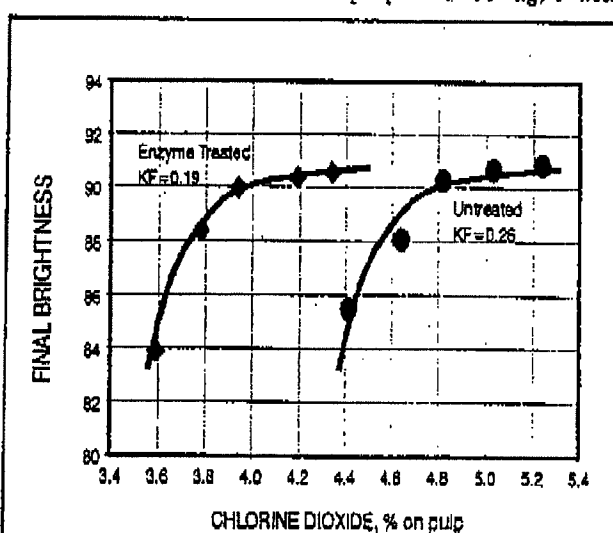
FIG. 7. THE EFFECT OF ENZYME TREATMENT ON CHLORINE DIOXIDE REQUIREMENTS IN A D(E₀)DED BLEACHING SEQUENCE. THE ENZYME TREATMENT WAS FOR 1 H WITH 500 ML ENZYME/t.

enzyme treatment.

Figure 5 illustrates the options for decreasing chemical requirements.

• *Chlorine savings:* A constant level of chlorine dioxide is used in the D_1 and D_2 stages while chlorine loadings are varied to maintain the same level of brightness with or without enzyme. To achieve 90 brightness with 13 kg ClO_2/t requires 60 kg Cl_2/t without enzyme treatment and 48 kg Cl_2/t with enzyme treatment. The chlorine decrease is 12 kg/t, or 20%. Decrease in chlorine can be expected to lower organo-chloride discharges and bleaching costs.

• *Chlorine dioxide savings:* By using enzyme treatment, a constant level of chlorine can be used while chlorine dioxide loadings in the D_1, and D_2 stages are decreased. To achieve 90 brightness with 60 kg Cl_2/t requires 13 kg ClO_2/t without enzyme treatment and 8 kg ClO_2/t with enzyme treatment. The chlorine dioxide savings is 5 kg/t (40%). Freed up chlorine dioxide generating capacity might then be used to increase the level of ClO_2 substitution in the (CD) stage, which might further enhance the bleaching [8].

• *Combined chlorine and chlorine dioxide savings:* An intermediate choice between the previous two options is to take a combination of chlorine and chlorine dioxide savings. This might lead to the lowest cost operation of the bleach plant with enzyme treatment. The choice of the lowest cost operating conditions depends on the relative cost of chlorine, chlorine dioxide, and alka-

li. The level of alkali is lessened by enzyme treatment in proportion to the decreased requirements of active chlorine in the (CD) stage.

SUBSTITUTION

The trend toward high levels of chlorine dioxide substitution in the chlorination stage has recently accelerated, due in part to environmental concerns over chlorine use. Preliminary testing of the effects of enzyme treatment on the chemical requirements in bleaching sequences with 50 and 100% chlorine dioxide substitution was carried out. The enzyme treatments were for one to two hours because this gives most of the benefit obtained with longer treatments, Fig. 5, and allows for flexibility in mill implementation.

Figure 6 shows the results of enzyme treatment followed by a (DC)(E_O)DED bleaching sequence, with 50% chlorine dioxide substitution in the (DC) stage. Enzyme-treated pulp requires 14 kg/t less total active chlorine to bleach to 90 brightness. The decrease in chemical usage is 16%. This decreased active chlorine requirement is a combination of decreased Cl_2 (from 30.7 kg/t to 25.0 kg/t)) and chlorine dioxide use (from 22.2 kg/t to 18.8 kg/t). The decrease in chemical requirements are of the same magnitude as those obtained with enzyme treatment followed by the (CD)EDED bleaching sequence with 10% chlorine dioxide substitution.

Figure 7 shows the results of enzyme

treatment followed by a $D(E_O)DED$ bleaching sequence, with 100% chlorine dioxide substitution. Enzyme treated pulp requires 15% less chlorine dioxide to bleach to 90 brightness; the enzyme treatment saves 7 kg ClO_2/t of pulp. The benefit of enzyme treatment is slightly greater than that obtained at 10% and 50% chlorine dioxide substitution.

CONCLUSIONS

Xylanase enzyme, used in a simple treatment of unbleached pulp, has the same delignification and brightening capability as 5 to 7 kg/t of ClO_2. The enzyme can be used to decrease the active Cl_2 used for the first stage of bleaching by 20% or decrease ClO_2 used in brightening by 5 kg/t.

Slightly greater benefits of enzyme treatment are obtained in bleaching sequences with high chlorine dioxide substitution. Depending upon the needs of a given mill, enzyme treatment could be used to decrease chlorination levels and thus AOX discharges, or to free up chlorine dioxide generation capacity.

REFERENCES

1. VIIKARI, L., RANUA, M., KANTELINEN, A., SUNDQUIST, J., LINKO, M. (1986). Bleaching with enzymes. Proc. Third Int. Conf. Biotech. in the Pulp and Paper Ind., Stockholm, p. 67.
2. KANTELINEN, D.A. (1988). Entsyymeillako eroon kloorista. Kamia-Kemi 9: 228-231.
3. PAICE, M.G., BERNIER, Jr., R., JURASEK, L. (1988). Viscosity-enhancing bleaching of hardwood kraft pulp by xylanase from a cloned gene. Biotechnol. Bioeng 32: 235-239.
4. KANTELINEN, D.A., RANUA, M., RATTO, M., VIIKARI, L., SUNDQUIST, J., LINKO, M. (1988). Hemicellulases and their potential role in bleaching. TAPPI Proceedings, 1988 International Pulp Bleaching Conference.
5. ERIKSSON, O., GORING, D.A.I., LINDGREN, B.O.. (1980). Structure studies on the chemical bonds between lignin and carbohydrates in spruce wood. Wood Sci. Technol. 14: 267-279.
6. VAHERI, M., MIIKI, K., JOKELA, V., KITUNEN, V., SALKINOJA-SALONEN, M. (1989). Bleaching of kraft pulp without formation of dioxin. Presented at Dioxin Conference, Toronto, September 21,1989.
7. AXEGARD, P. (1984). Effect of ClO_2-substitution on bleaching efficiency and the formation of organically bound chlorine-part 1. TAPPI Proceedings, 1984 TAPPI Pulping Conference.
8. FORBES, D.R. (1988). TAPPI Notes, 1989 Bleach Plant Operations Seminar, p. 11-19.
9. ANNERGREN, C.E., LINDSTROM, L., LINDBLAD, P., NORDEN, S. (1988). Effect of oxygen bleached kraft pulp. TAPPI Proceedings. 1988 International Pulp Bleaching Conference.

Résumé: L'enzyme xylanase, utilisé dans un traitement simple de la pâte non blanchie, offre les mêmes avantages de brillance et de délignification efficace que 5 à 7 kg/tonne de $ClO2$. Lors du blanchiment conventionelle (CD)EDED, l'enzyme peut être utilisé pour diminuer de 20% le $Cl2$ actif utilisé pour le premier stade du blanchiment, ou pour diminuer de 5 kg/tonne le $ClO2$ utilisé pour la brillance de la pâte. On obtient des résultats sensiblement meilleurs du traitement aux enzymes dans les séquences de blanchiment dont le remplacement de bioxyde de chlore est élevé. Selon les besoins d'une usine donnée, le traitement aux enzymes pourrait être utilisé pour diminuer les niveaux de chloration, et par conséquent, les rejets de COHA (composés organiques halogénés adsorbables), ou pour libérer la capacité de génération de bioxyde de chlore.

Abstract: Xylanase enzyme, used in a simple treatment of unbleached pulp, has the same effective delignification and brightening benefits as 5 to 7 kg/t of chlorine dioxide (ClO_2). When bleaching to 90 (ISO) brightness with the (CD)EDED conventional bleach sequence, the enzyme can be used to decrease the active Cl_2 used for the first stage of bleaching by 20% or decrease ClO_2 used in brightening by 5 kg/t. Slightly greater benefits of enzyme treatment are obtained in bleaching sequences with high chlorine dioxide substitution. Depending upon the needs of a given mill, enzyme treatment could be used to decrease chlorination levels and thus AOX discharges or to free up ClO_2 generation capacity.

Pulps", *Trans. Tech. Sect., CPPA* 5(4):TR92–99 (1979).

5. LINDHOLM, C.A., "Comparison of Some Papermaking Properties of Groundwood, Pressure Groundwood and Thermomechanical Pulp by Means of Artificial Blends of Pulp Fractions. Part 2. The Fines Fraction", *Papari Ja Puu* 62(12):803–808 (1980).

6. WOOD, J.R. and KARNIS, A., "The Determination of the Specific Surface of Mechanical Pulp Fines from Turbidity Measurements", Proc. Intl. Paper Physics Conf., 2:655–661 (1991).

7. KARNIS, A., "Effect of Wood Species and Process on Linting Propensity and Fibre Roughening of Mechanical Pulps", *J. Pulp Paper Sci.* 21(9):J321–J329 (1995).

8. de MONTMORENCY, W.H., "The Longitudinal Grinding of Wood", *Pulp Paper Mag. Can.* (C):197–208 (1947).

9. VON ALFTHAN, G., "Influence of the Positioning of the Wood", *Revue A.T.I.P.* 24(6):241–259 (1970).

Bleachability Improvements of Kraft Pulp by Alkaline Leaching and Xylanase Treatment

J. LI, M.G. PAICE, J.M. MacLEOD, and L. JURASEK

The bleachability of softwood kraft pulp can be improved by xylanase treatment or by alkaline leaching. When used sequentially, the two processes do not complement each other in improving bleachability, so combining them is not recommended. Their mechanisms have been investigated by analyzing the removal of hemicellulose and lignin during the treatments. Whether by alkaline leaching or xylanase treatment, the improvement in bleachability results from reducing the restricting role that hemicelluloses play in the removal of lignin macromolecules. However, the mechanisms are not exactly the same; xylanase specifically hydrolyzes xylan, while alkaline leaching randomly extracts short-chain carbohydrates and lignin.

J. LI, M.G. Paice,
J.M. MacLeod and L. Jurasek
Paprican
570 St. John's Blvd.
Pointe Claire, QC
H9R 3J9

INTRODUCTION

Concern about chlorinated organic compounds has prompted the pulp and paper industry to reduce the use of chlorine and chlorine compounds in pulp bleaching. Methods of decreasing the use of these chemicals include: (a) reducing the lignin content of the brownstock entering the bleach plant, such as by extended pulping [1–3], and by alkaline leaching [4]; (b) improving the bleachability of the pulps, such as by xylanase treatment [5,6]; and (c) using alternative bleaching reagents, such as oxygen, ozone, peroxide, etc. [7–10].

Recently, we demonstrated that 20–30% of the residual lignin can be leached from water-washed, unbleached kraft pulps in less than 1 h using 0.1–1.0 mol/L NaOH at 100°C [4,11]. This fast leaching rate was explained by invoking reversible lignin association phenomena known for almost three decades [12,13]. Enhanced lignin removal during washing at elevated pHs has also been reported by others [14,15], but was probably in part due to other effects. In one case, the rate of alkaline degradation

reaction of lignin was still significant at 150°C [14]. In the other [15], the air in their system could have led to oxygen delignification.

The ability of xylanase enzyme to improve the bleachability of pulps during subsequent chemical bleaching was first reported in 1986 [16], and several mills are now using the technology routinely [6,17]. The improved bleachability that results from partial hydrolysis of xylan can be explained in various ways, and is still a subject of debate. At least three explanations have been proposed: (1) increased fibre swelling [18]; (2) cleavage of lignin-carbohydrate linkages [16]; and (3) specific hydrolysis of reprecipitated xylan, causing an increase in pore size in the hemicellulose matrix [19–21]. Any of these three effects, or a combination of them, would result in faster diffusion of residual lignin from the fibre walls, and thereby more rapid bleaching. We thought that an experimental comparison of alkaline leaching to enzymatic hydrolysis would provide a better understanding of the function of hemicelluloses during bleaching, because both
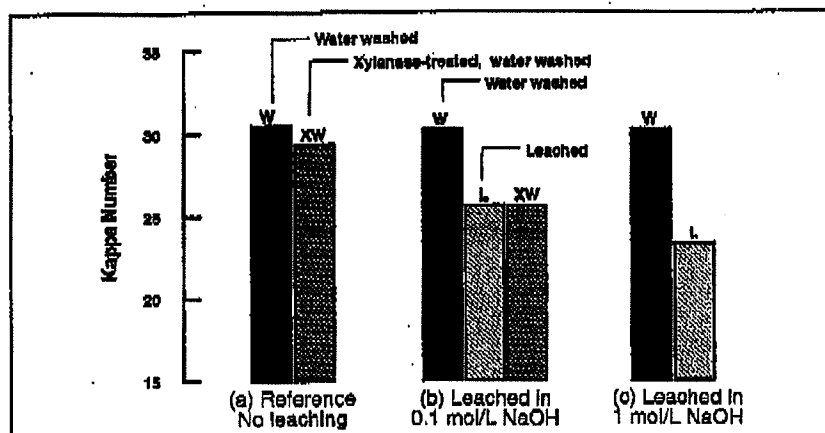
Fig. 1. The kappa numbers of a softwood kraft pulp after each sequential treatment. In group (a), pulp was treated with xylanase and washed. In group (b), pulp was leached in 0.1 mol/L NaOH, and then treated with xylanase. In group (c), pulp was only leached in 1.0 mol/L NaOH.

treatments are known to affect the carbohydrate fraction.

EXPERIMENTAL PROCEDURES

The pulp sample used in the leaching experiments was obtained by cooking black spruce chips of between 2 and 12 mm thickness to 1600 H-factor in a 20 L digester with forced liquor circulation. The pulping conditions were: 18% active alkali (as Na_2O, on oven-dry wood), 30% sulphidity, 90 min to 170°C, liquor:wood of 4:1 L/kg. Half of the cooked chips were disintegrated in tap water and rinsed in it until the filtrate was clear. After being left in cold water overnight at 1% consistency, the pulp was screened on a vibrating flat screen with 0.25 mm slots, and was thickened to 35% consistency prior to storage at 4°C. The other half of each batch of cooked chips was processed in the same way, but with deionized water. The pulp washed with tap water was used as the reference sample, and the pulp washed with deionized water was the starting sample for the alkaline leaching experiments. The kappa numbers of the pulps washed with tap water and deionized water were 30.5 and 30.2, respectively. It was observed previously that the kappa numbers of pulps washed with tap water were generally higher than those of pulps washed with deionized water. The difference can be as much as two kappa units, depending on the tap water quality. However, because the difference was small in this case, no distinction was made between pulps washed with tap water or deionized water.

Alkaline leaching experiments were performed in 4000 mL Erlenmeyer flasks at 1% pulp consistency [4]. The pulp sample was mixed with pre-boiled, deionized water, and nitrogen was bubbled through the suspension for 10 min to remove all oxygen. Alkaline leaching was initiated by adding boiled, concentrated caustic solution to the suspension to reach a final concentration of either 0.1 or 1.0 mol/L NaOH. During leach-

ing experiments, nitrogen was bubbled through the leaching solution to eliminate oxygen, and gentle agitation was provided by a magnetic stirrer. Pulp samples were leached for either 1 h with 0.1 mol/L NaOH, or 30 min with 1.0 mol/L NaOH at 100°C [4].

After leaching, the pulp samples were washed with deionized water, dried in air, and analyzed for kappa number and viscosity, as well as for carbohydrates by hydrolysis and gas chromatography (TAPPI Method T 249) and for pentosans (Technical Section, CPPA Standard Testing Method G.12). The leaching liquors were analyzed for lignin by UV spectrophotometry, and for carbohydrate concentration by the modified anthrone method [22].

The xylanase treatment of the reference and leached pulps was performed with 25 U/g of xylanase (Pulpzyme HB, Novo-Nordisk, Copenhagen) at 10% consistency for 2 h at 50°C. One unit (U) is defined as the amount of enzyme that produces 1 μmol of xylose per minute from larchwood xylan [20]. The pH was initially adjusted to 4.5 with sulphuric acid; after treatment, the pH was between 5 and 6. Subsequent bleaching was performed without washing the pulp.

The effect of sequential alkaline leaching and xylanase treatment was examined by testing the bleachability of the reference, alkaline leached, and xylanase-treated pulps in a conventional CₙE sequence. Chlorination was performed with a mixture of 80% Cl_2 and 20% ClO_2, using an active chlorine multiple of 0.17 (i.e. 0.17 × kappa number). Treatment was for 30 min at 50°C and a pulp consistency of 3.5%. Caustic extraction was done with an NaOH charge of 0.11 × kappa number at 70°C for 90 min.

The molecular weight distribution of the lignin was analyzed at pH 13 by the gel permeation chromatography method developed by Sarkanen et al. [13]. A 70 × 2.5 cm column was packed with swollen Sephadex G100 (a cross-linked dextran gel from Phar-

macia). Carbonate-free 0.1 mol/L NaOH was used as the eluent. The column was calibrated with polystyrene sulphonate (PSS) standards. The calibration curve for kraft lignin molecular weight (M_w) versus relative retention volume (V_r) was obtained by multiplying the molecular weight of PSS by a factor of 1.7 [13].

RESULTS AND DISCUSSION

Kappa Number Reduction by Alkaline Leaching and Xylanase Treatment

Figure 1 shows the kappa numbers of the reference pulps, the pulps leached with 0.1 and 1.0 mol/L NaOH, and the xylanase-treated pulps. Deionized water was always used in the washing after xylanase treatment. As we showed previously [11], a significant amount of lignin can be removed during alkaline leaching, even with the pulps that had stood overnight in deionized water. The kappa numbers were reduced by 15% and 23% after leaching with 0.1 and 1.0 mol/L NaOH, respectively. Since the bleaching chemical charge is based on pulp kappa number, the kappa number reduction obtained by alkaline leaching gives the percentage savings in bleaching chemicals.

To obtain a better understanding of the effect of xylanase treatment on enhanced bleachability, the kappa numbers of pulps after xylanase treatment and washing were measured. The kappa number of the reference pulp after xylanase treatment and washing dropped to 28.6, a 6% decrease (Fig. 1). Since the bleaching chemical charge is normally based on the kappa number before xylanase treatment (i.e. the kappa number of the washed pulp), it is likely that a part of the bleaching chemical saving or improved bleachability is due to the reduced kappa number, or more specifically, removal of part of the lignin before bleaching. Xylanase treatment removed practically no lignin from the 0.1 mol/L NaOH alkaline-leached pulp, however, as shown by comparison of the kappa numbers in Fig. 1b.

Effect of Xylanase Treatment and Alkaline Leaching on Bleachability

Three pulps, a water-washed reference pulp and pulps leached with 0.1 and 1.0 mol/L NaOH, were tested to determine the effect of xylanase treatment on bleachability (Fig. 2). Each pulp was divided into two parts. One part was treated with xylanase, and then CₙE bleached. The other part, serving as a control, was bleached under the same conditions, but without xylanase treatment. Figure 2 shows the kappa numbers of the pulps after CₙE bleaching.

Three observations can be made. First, the difference between the CₙE kappa numbers of the reference and xylanase-treated pulps was smaller if the pulps were leached. In fact, after leaching with strong caustic (1.0 mol/L NaOH), the effect of
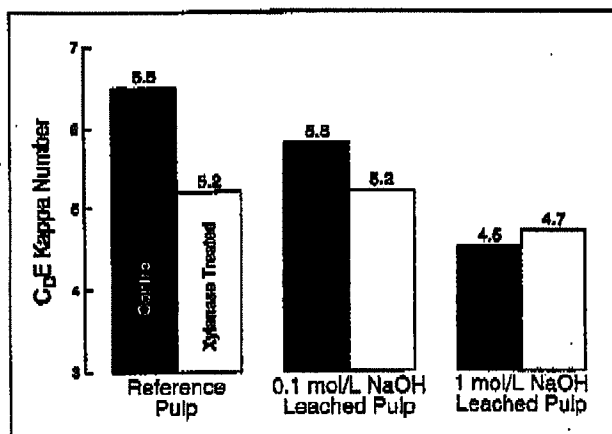
Fig. 2. The CpE kappa numbers of the pulps with or without xylanase treatment. There are three pulps: the reference pulp, without leaching treatment; the pulp leached in 0.1 mol/L NaOH; and the pulp leached in 1.0 mol/L NaOH.
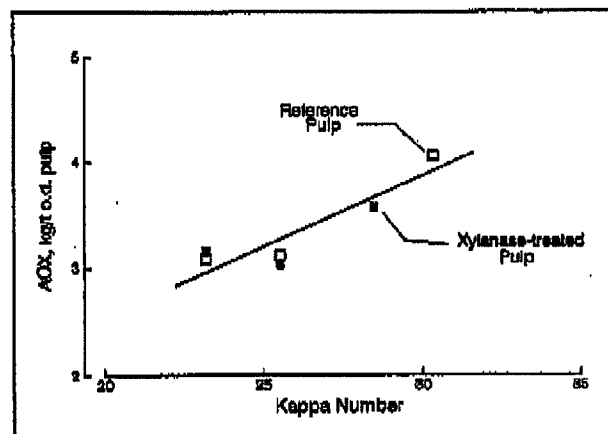
Fig. 3. AOX production as a function of the kappa number before bleaching. □ – reference pulps; ■ – xylanase-treated pulps.

xylanase treatment completely disappeared. Second, compared to the unleached reference pulps, the alkaline-leached reference pulps had lower C_DE kappa numbers, indicating that alkaline-leached pulps are also easier to bleach. The stronger the caustic used in leaching, the lower the C_DE kappa number reached. Finally, the C_DE kappa numbers of the two xylanase-treated pulps, the unleached and 0.1 mol/L alkaline-leached, were about the same, while the 1.0 mol/L alkaline-leached pulp had a slightly lower C_DE kappa number.

Based on these results, it appears that there is a limit to the bleachability improvement which can be obtained from combined alkaline leaching and xylanase treatments. If an improvement has already been partly achieved by alkaline leaching, xylanase treatment can deliver only the remaining part of the effect achieved when xylanase is used alone. In the extreme case, leaching with strong alkali can make xylanase treatment

redundant. Thus, the effects of xylanase treatment and alkaline leaching on bleachability are not complementary, i.e. their sequential use would be ineffective.

Figure 3 shows AOX production during CDE bleaching as a function of unbleached kappa number. As expected, AOX decreased linearly with decreasing initial kappa number. There was no difference in AOX formation between the reference and xylanase-treated pulps.

Analysis of Hemicellulose Removed with Lignin

The fact that leaching with strong enough alkali can achieve the same results as xylanase treatment suggests that hemicelluloses and lignin are both affected by alkaline leaching. On the other hand, xylanase treatment degrades xylan and, as a result, to a limited extent helps remove lignin. What are the similarities and differences between the two processes?

To investigate the effect of alkaline leaching on hemicellulose extraction, the polysaccharide contents of the pulps treated under different conditions were measured by acid hydrolysis followed by gas chromatography. The results are listed in Part I of Table I. Arabinan and galactan were not detected in any of the samples. Each sample was analyzed in duplicate. The analyses of the first two samples were repeated again in duplicate. The averages and differences are listed. To make comparison easier, all results are also reported on the basis of total carbohydrate content (column 6), and these normalized results are listed in brackets below the original data.

The initial washed pulp had somewhat higher xylan and mannan content than all the other samples, while the bleached pulps had the lowest amounts of hemicellulose. Nevertheless, the accuracy and reproducibility of the analyses do not allow a firm conclusion to be drawn, because the error associated with each value is comparable to the magnitude of the difference between samples.

For a more accurate estimate of hemicellulose contents, the pentosan content of each pulp was measured; the results are listed in Part II of Table I. The numbers in brackets are the pentosan contents recalculated on the basis of carbohydrate contents; in each case, this is the difference between the total pulp (100%) and its lignin content calculated as kappa number × 0.147. Apart from the sample leached in 1.0 mol/L NaOH, the pentosan contents of the samples were quite close. This suggests that neither alkaline leaching with 0.1 mol/L NaOH nor xylanase treatment under these experimental conditions affects the hemicellulose content significantly. Alkaline leaching with 1.0 mol/L NaOH, however, did remove about 20% of the total pentosans. Assuming that the percentage of mannan removal is about the same, the total carbohydrate loss (or yield loss) by alkaline leaching in 1.0 mol/L

TABLE I. CARBOHYDRATE ANALYSIS OF THE PULPS

		Part I				Part II
Sample	Kappa Number	Xylan (%)	Mannan (%)	Glucan (%)	Total (%)	Pentosans (%)
W	30.8	8.7±0.5 (9.9)	5.8±0.1 (6.6)	78.7±2.0 (85.8)	88.2±2.6 (100)	9.54 (9.99)
WL	26.7	7.2±0.3 (8.0)	5.0±1.0 (5.6)	77.2±1.5 (86.4)	89.4±2.8 (100)	9.75 (10.1)
WL(0.1)X	24.9	8.1 (8.4)	5.7 (5.9)	82.8 (85.7)	96.6 (100)	9.24 (9.58)
WL(0.1)XL(0.1)	23.5	8.3 (8.7)	5.5 (5.8)	81.6 (85.5)	95.4 (100)	9.73 (10.1)
WL(0.1)B	5.7	7.3 (7.2)	5.8 (5.7)	89.0 (87.2)	102 (100)	9.66 (9.64)
WL(1.0)B	4.0	7.5 (7.5)	4.4 (4.4)	87.5 (88)	99.4 (100)	7.69 (7.74)

Note: In the sample name, W, L, X and B stand for washed, leached, xylanase-treated, and bleached, respectively, and the number following L is the caustic concentration used during leaching.
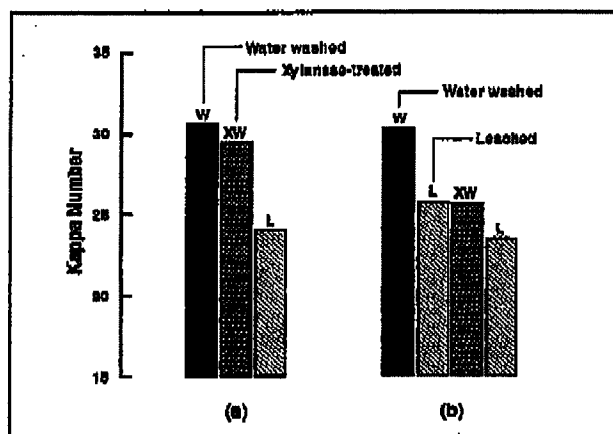
Fig. 4. Kappa numbers of the pulps after each sequential treat-ment. In group (a), pulp was treated with xylanase (X), washed (W), and then leached (L) in 0.1 mol/L NaOH. In group (b), pulp was leached in 0.1 mol/L NaOH, then xylanase treated and washed, finally, leached in 0.1 mol/L NaOH again.
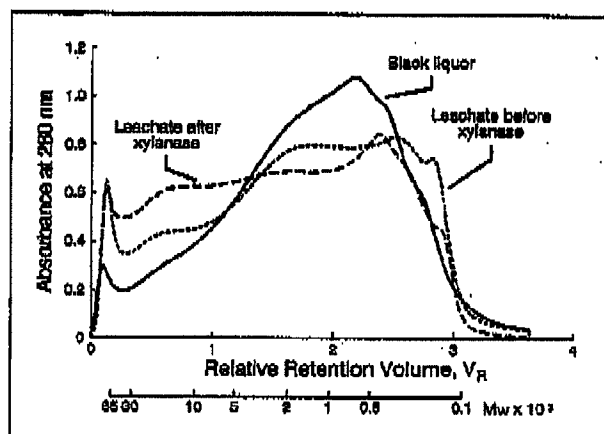
Fig. 5. The molecular weight distributions of lignin in the leachates (and in black liquor) at 280 nm.

NaOH is about 3% on pulp or 1.5% on wood, which is about the same as was previously calculated [11] from the measurement of α, β, γ cellulose fractions (Technical Section CPPA Standard Testing Method G.29P).

The results in Table I show that the reproducibility and accuracy of the carbohy-drate analyses of the pulp samples do not allow accurate measurement of small differ-ences in pulp hemicellulose content result-ing from xylanase treatment and alkaline leaching with 0.1 mol/L NaOH. In another approach, the sugar contents of some of the leaching liquors were analyzed by the modi-fied anthrone method [22]; these data are shown in Table II. Note that the absolute value obtained by this method may not be accurate because it uses only one sugar, xylose, to calibrate all the sugars. Also, the intensity of the colour was slightly affected by the presence of small amounts of lignin and hydroxy-acids. If it is assumed that this is a systematic error, the relative ratios of total sugar contents of the samples can be considered to be very close to the true ratios.

The results in Table II indicate that alkaline leaching with 0.1 mol/L NaOH extracted a small amount of hemicellulose, which probably leads to the improved bleachability shown in Fig. 2. The additional xylanase treatment before alkaline leaching increased the amount of carbohydrate extracted during alkaline leaching, as expected. Carbo-hydrate extraction by leaching with 1.0 mol/L NaOH was much more severe than that with 0.1 mol/L NaOH, confirming the result of

the pentosan analysis shown in Table I. With the data in Table II, a rough estimate of carbohydrate loss during the alkaline leach-ing can be made. Leaching in 0.1 mol/L NaOH led to 0.3% of carbohydrate loss based on pulp. Xylanase treatment resulted in an additional 0.2% carbohydrate loss. Leaching in 1.0 mol/L NaOH, however, ex-tracted 4.7% of the carbohydrate from the pulp. These values agree well with those measured previously, at least in the order of magnitude [20,23]. It is believed that these carbohydrate losses are mainly hemicellu-lose. A hemicellulose loss in the order of 0.5% on pulp (or 0.25% on wood) generally does not affect pulp properties very much. Extraction of 4.7% hemicellulose from the pulp (~2.3% on wood), however, will sig-nificantly affect the pulp beatability [11]. These treatments should not decrease the pulp strength.

Comparing the data in Tables I and II, the sensitivity of the carbohydrate analyses is much better with liquor samples. The large amount of carbohydrate removed, the com-pletely eliminated effect of xylanase treat-ment, and the improved bleachability found with the pulps leached in 1.0 mol/L NaOH suggest that pulp bleachability is related to the hemicellulose content of the pulp.

Based on these carbohydrate analyses, we can conclude that improved bleachability after alkaline leaching occurs because some hemicelluloses were extracted along with lignin during the leaching. The stronger the caustic used in leaching, the more hemicel-lulose is extracted, making it easier for lignin to diffuse from fibre walls during bleaching. When the hemicellulose removal by leach-ing is beyond what can be achieved by xyla-nase treatment, then xylanase will have no additive effect on pulp bleachability. In fact, the improvement in bleachability can be even greater than that obtained by xylanase treatment, as was shown in Fig. 2 for the

pulp leached with 1.0 mol/L NaOH. Leach-ing takes out mannan also, and it is interest-ing to note that mannan hydrolysis by mannanase also improves bleachability [20].

Effect of Xylanase Treatment on Lignin Removal in Alkaline Leaching

To examine the effect of xylanase treatment on lignin removal in alkaline leaching, pulps after xylanase treatment were leached in 0.1 mol/L NaOH. The kappa numbers after leaching are shown in Fig. 4. If pulp is first treated with xylanase, more lignin can be removed during alkaline leach-ing — the kappa number of W-XW-L is lower than that of W-L. The effect of xylan depolymerization on lignin removal is fur-ther illustrated by the fact that xylanase treat-ment of the previously leached pulp, W-L, liberated more lignin from the pulp in further leaching (W-L-XW-L).

The way that xylanase treatment affects lignin removal can also be seen in the molecular weight distributions of dissolved lignin in the leachates. Figure 5 shows these distributions in the leachates of W-XW-L and W-L. As a comparison, the molecular weight distribution of lignin in black liquor is also shown in Figure 5. The profiles are normalized, based on the same total lignin mass measured at 280 nm.

The distribution profiles indicate that the leachates contain more high molecular weight lignin (>5000) than black liquor does. Xylanase treatment, or xylan degrada-tion, leads to even greater removal of high molecular weight lignin; this might result from xylan degradation clearing a path (i.e. pores in fibre walls) to allow faster diffusion of the larger lignin macromolecules. A simi-lar effect was reported recently by Kan-telinen et al. [21].

From the data in Figs. 4 and 5, we can

TABLE II.
SUGAR CONTENT OF LEACHING LIQUORS

Sample	Sugar (mg/L)
WL (0.1)	30
WXL (0.1)	49
WL (1.0)	470

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a) With O₂ stage

b) Without O₂ stage, with extended delignification

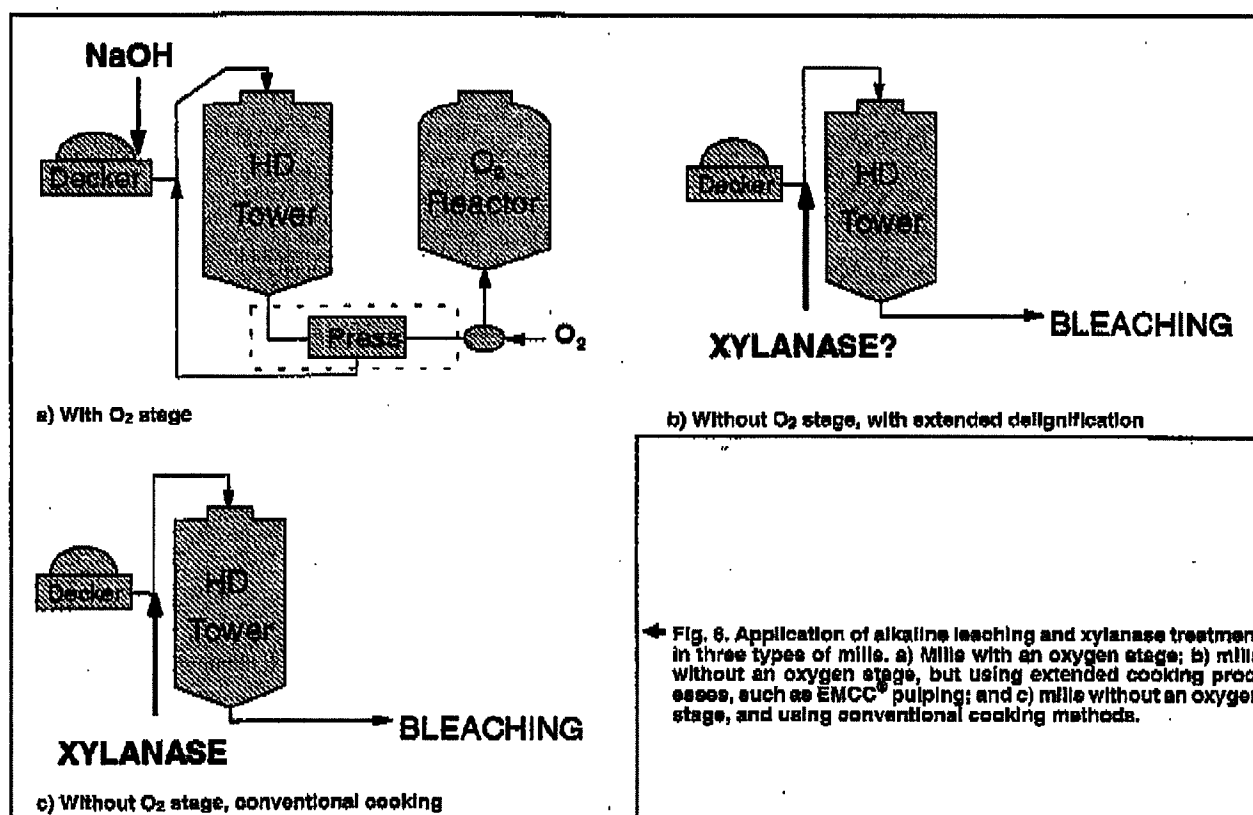c) Without O₂ stage, conventional cooking

Fig. 6. Application of alkaline leaching and xylanase treatment in three types of mills. a) Mills with an oxygen stage; b) mills without an oxygen stage, but using extended cooking processes, such as EMCC® pulping; and c) mills without an oxygen stage, and using conventional cooking methods.

conclude that xylan degradation resulting from xylanase treatment leads to greater removal of lignin macromolecules, especially those of higher molecular weight. Therefore, the improved bleachability of kraft pulps after xylanase treatment results mainly from reduced restriction of lignin diffusion. Xylan degradation may also release lignin bound with xylan in lignin-carbohydrate complexes, but this would not necessarily result in release of higher molecular weight lignin. Since the gel permeation fractions would include the weight of carbohydrate material in solubilized lignin-carbohydrate complexes, it could be argued that more low molecular weight lignin should be seen if cleavage of lignin-carbohydrate complexes was a significant factor.

Based on our experimental results, we propose the following mechanisms of alkaline leaching and xylanase treatment. Alkaline leaching not only removes lignin, but also extracts the relatively low molecular weight hemicelluloses. Thus, alkaline leaching will allow a reduced bleaching chemical charge, and a lower kappa number after bleaching or improved bleachability. The effect of xylanase treatment, however, can be seen mainly from a lower kappa number after bleaching, i.e. improved bleachability, because the kappa number after the treatment and water washing changes only slightly. The improved bleachability after alkaline leaching or xylanase treatment results from reducing the restricting role that

hemicelluloses play in the removal of lignin macromolecules. The mechanisms are not exactly the same: xylanase specifically hydrolyzes xylan, while alkaline leaching randomly extracts short-chain carbohydrates.

INDUSTRIAL IMPLICATIONS

The changes in kappa number after C$_D$E bleaching (Fig. 2) indicate that the effects on bleachability of alkaline leaching followed by xylanase treatment are not complementary. Therefore, the sequential application of the two processes, alkaline leaching followed by xylanase treatment, will not produce an extra benefit.

Combining the lower charge of bleaching chemicals and the improved bleachability, the total savings of bleaching chemicals in the case of alkaline leaching with 0.1 mol/L NaOH may be somewhat higher than those achieved with xylanase treatment without leaching. However, which treatment should be used in a specific mill depends on the configuration of the fibre line.

According to their pulping and bleaching methods, most kraft mills can be divided into three categories, as shown in Fig. 6: (a) mills with oxygen stage; (b) mills without oxygen stage, but using extended cooking processes, especially EMCC® process; and (c) mills without oxygen stage, and using conventional cooking methods.

In the first scenario, i.e. mills with oxygen stages, it would be beneficial to

operate the whole brownstock washing line at a higher pH. No additional caustic, other than the normal NaOH charge for the O$_2$ stage, is required if the process is modified as shown in Fig. 6a. NaOH required for the O$_2$ stage is charged before the high-density (HD) storage tower, which provides the conditions for alkaline leaching to take place. In the case of a high-consistency O$_2$ stage, the pressate is recycled to the HD tower. With 2% NaOH charge on pulp for a 35% consistency O$_2$ stage, the NaOH concentration in HD tower can be built up to 0.2 mol/L. In the case of a medium-consistency O$_2$ stage, similar process modifications involving a decker can also provide relatively high NaOH concentrations in the HD tower without significant additional NaOH. The capital cost for the process modification should be very minimal. Xylanase treatment is not recommended before the oxygen stage, but could be used after the oxygen stage to provide additional improvement in C$_D$E bleachability [24].

In the second scenario, mills operating under extended delignification conditions (e.g. an EMCC® process) may not benefit significantly from xylanase treatment because the hemicellulose content in the pulp could be reduced by the high alkali concentration near the end of cooking. This conclusion remains to be tested with the various EMCC® regimes, although, in general, we suggest that any pulping process which affects hemicelluloses in a manner similar to

that of alkaline leaching may not significantly benefit from subsequent xylanase treatment.

Finally, mills with conventional kraft pulping (both continuous and batch) and without an oxygen stage should obtain a significant reduction of bleaching chemical consumption by installing xylanase treatment. The economics of the xylanase treatment is well justified by the savings in bleaching chemical when high chlorine dioxide substitution is in use [25].

CONCLUSIONS

The bleachability of softwood kraft pulp can be improved by xylanase treatment or by alkaline leaching. In addition, with alkaline leaching, a significant kappa number reduction, and thus a reduced initial bleaching chemical charge, can be achieved. The mechanisms of the two processes have been investigated by analyzing the removal of hemicellulose and lignin during the treatments. The effects of the processes on bleachability are not complementary, because the mechanisms are similar: hydrolysis of xylan or extraction of the hemicelluloses reduces the restriction of hemicellulose on removal of lignin macromolecules. Thus, combining the two processes is not recommended.

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REFERENCES

1. JOHANSSON, B., MJOBERG, J., SANDSTROM, P. and TEDER, A., "Modified Continuous Kraft Pulping — Now a Reality", *Svensk Papperstidn.* 10:30 (1984).
2. ANDREWS, E.K., "RDH Kraft Pulping — Liquor Profiling to Extend Delignification, Decrease Effluent Liability and Improve Productivity and Pulp Properties", TAPPI Pulping Conf., 607 (1989).
3. PURSIAINEN, S., HILJANEN, S., UUSITALO, P., KOVASIN, K. and SAUKKONEN, M., "Mill-Scale Experiences of Extended Delignification with SuperBatch Cooking Method", *Tappi J.* 73(8):115 (1990).
4. LI, J. and MacLEOD, J.M., "Alkaline Leaching of Kraft Pulps for Lignin Removal", *J. Pulp Paper Sci.* 19(2):J85 (1993).
5. VIIKARI, L., SUNDQUIST, J. and KETTUNEN, J., "Xylanase Enzymes Promote Pulp Bleaching", *Paperi ja Puu* 73:384 (1992).
6. REID, I.D. and PAICE, M.G., "Biological Bleaching of Kraft Paper Pulp" in Frontiers of Industrial Mycology, G.J. Leatham, Ed., Chapman Hall Publisher, 112 (1992).
7. WALDESTAM, S., JAMIESON, A. and ALMBERG, L., "Oxygen Bleaching Shows Potential for Reducing Costs, Effluent Problems", *Pulp & Paper* 54(3):92 (1980).
8. HSU, C.L. and HSIEH, J.S., "Advantages of Oxygen vs. Air in Delignifying Pulp", *Tappi J.* 69(4):125 (1986).
9. LAXEN, T., RYYNANEN, H. and HENRICSON, K., "Medium-Consistency Ozone Bleaching", *Paperi Ja Puu* 72:90 (1990).
10. COLODETTE, J.L., SINGH, U.P., GHOSH, A.K. and SINGH, P.R., "Ozone Bleaching Research Focuses on Reducing High Cost, Poor Selectivity", *Pulp & Paper* June:139 (1993).
11. LI, J. and MacLEOD, J.M., "The Effect of Alkaline Leaching on Pulp Bleachability and Physical Properties.", *Tappi J.* 75(12):159 (1993).
12. BENKO, J., "The Measurement of Molecular Weight of Lignosulfonic Acids and Related Materials by Diffusion. IV", *Tappi* 47(8):508 (1964).
13. SARKANEN, S., TELLER, D.C., ABRAMOWSKI, E. and McCARTHY, J.L., "Lignin 19. Kraft Lignin Component Conformation and Associated Complex Configuration in Aqueous Alkaline Solution", *Macromolecules* 15(4):1098 (1982).
14. HENRICSON, K., PIKKA, O., VILPPONEN, A. and VIRKOLA, N., "Method of Intensifying the Washing of a Fibre Suspension", A. Ahlstrom Corp. (Finland), US Patent, No. 4,971,658 (Issued Nov. 20, 1990).
15. SMITH, A.J., GUSTAFSON, R.R. and McKEAN, W.T., "Enhanced Lignin Removal in Brown Stock Washing", *Tappi J.* 76(6):81 (1993).
16. VIIKARI, L., RANUA, A., KANTELINEN, A., LINKO, M. and SUNDQUIST, J., "Bleaching with Enzymes" in Biotechnology in the Pulp & Paper Industry, Proc. 3rd Intl. Conf., Stockholm, 67 (1986).
17. SCOTT, B.P., YOUNG, R.S. and PAICE, M.G., "Mill-Scale Enzyme Treatment of a Softwood Kraft Pulp Prior to Bleaching", *Pulp Paper Can.* 94(3):57 (1993).
18. CLARK, T.A., STEWARD, D., BRUCE, M.E., McDONALD, A.G., SINGH, A.P. and SENIOR, D.J., "Improved Bleachability of Radiata Pine Kraft Pulps Following Treatment with Hemicellulolytic Enzymes", *Appita* 44:389 (1991).
19. KANTELINEN, A., HORTLING, B., SUNDQUIST, J., RANUA, M., VIIKARI, L. and LINKO, M., "The Role of Reprecipitated Xylan in the Enzymatic Bleaching of Kraft Pulp", Proc. 6th Intl Symp. Wood Pulping Chem., Melbourne, 493 (1991).
20. PAICE, M.G., GURNAGUL, N., PAGE, D.H. and JURASEK, L., "Mechanism of Hemicellulose-Directed Bleaching of Kraft Pulps", *Enzyme Microbial. Technol.* 14:272 (1992).
21. KANTELINEN, A., HORTLING, B., SUNDQUIST, J., LINKO, M. and VIIKARI, L., "Proposed Mechanism of the Enzymatic Bleaching of Kraft Pulp with Xylanase", *Holzforschung* 47:318 (1993).
22. BAILEY, R.W., "The Reaction of Pentoses with Anthrone", *Biochem. J.* 68:669 (1958).
23. ALLISON, R.W., CLARK, T.A. and ELLIS, M.J., "Process Effects on the Response of Softwood Kraft Pulp to Enzyme-Assisted Bleaching", Proc. TAPPI Intl. Pan Pacific Conf., 49 (1994).
24. DU MANOIR, J.R. and DUBELSTEN, P., "Oxygen Delignification and Enzyme Treatment", European Patent Application, No. 90301379.5 (1990).
25. TOLAN, J., OLSON, D. and DINES, R., "Survey of Xylanase Enzyme Usage in Bleaching in Canada", *Pulp Paper Can.* 96(12):T403 (1995).

ABSTRACT: The bleachability of softwood kraft pulp can be improved by xylanase treatment or by alkaline leaching. When used sequentially, the two processes do not complement each other in improving bleachability, so combining them is not recommended. Their mechanisms have been investigated by analyzing the removal of hemicellulose and lignin during the treatments. Whether by alkaline leaching or xylanase treatment, the improvement in bleachability results from reducing the restricting role that hemicellulose plays in the removal of lignin macromolecules. However, the mechanisms are not exactly the same; xylanase specifically hydrolyzes xylan, while alkaline leaching randomly extracts short-chain carbohydrates and lignin.

RESUME: L'aptitude au blanchiment de la pâte kraft de résineux peut être améliorée par un traitement au xylanase ou par la lixiviation alcaline. Lorsqu'ils sont utilisés de façon séquentielle, ces deux procédés ne sont pas complémentaires en termes d'amélioration de l'aptitude au blanchiment de la pâte, de sorte que leur utilisation combinée n'est pas souhaitable. Nous avons étudié les mécanismes de ces procédés en analysant les modalités d'élimination de l'hémicellulose et de la lignine en cours de traitements. Que l'on fasse appel à la lixiviation alcaline ou au traitement au xylanase, l'amélioration de l'aptitude au blanchiment découle de la réduction du rôle restrictif que les hémicelluloses jouent dans l'élimination des macromolécules de la lignine. Nous nous devons de signaler que ces mécanismes ne sont pas exactement les mêmes: d'une part la xylanase hydrolyse le xylane, tandis que la lixiviation alcaline extrait aléatoirement les hydrates de carbone à chaînes courtes et la lignine.

KEYWORDS: SOFTWOOD PULPS, KRAFT PULPS, BLEACHABILITY, KAPPA NUMBER, DELIGNIFICATION, REMOVAL, HEMICELLULOSES, XYLANS, LIGNINS, LEACHING, XYLANASE.

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PULP AND PAPER MANUFACTURE

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Edited by

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Department of Paper Science & Engineering
University of Wisconsin at Stevens Point, U.S.A.

and

Al Wong, *P.E., Specialist Technology Management*
Arbokem, Inc., Montreal, Quebec, Canada

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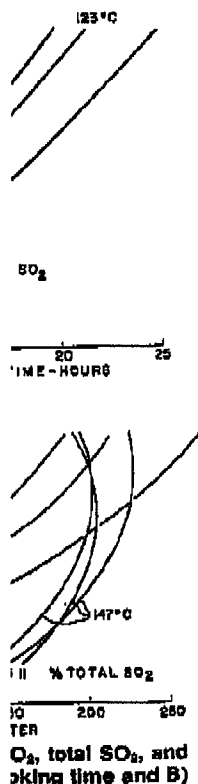
re-condensation and liquor breakdown (sulfate formation), the major reason for uncontrolled cellulose degradation.

Table 61A summarizes the results of optimizing the three parameters for three levels of combined SO₂ in the cooking liquor. Improved acetylation pulp quality is achieved with decreasing concentration of any of the four bases (Ca^{++}, Mg^{++}, NH_4^+, and Na^+) commonly employed in acid bisulfite pulping. There is evidence, however, that the bivalent alkaline earth cations cause a greater improvement in quality than the monovalent alkali cations. Apart from acetylation grade pulp, beneficial effects on the properties of other types of dissolving pulp are also found.

2. Prehydrolysis

Prior to 1950, dissolving grade pulps were produced almost exclusively by the sulfite process [26]. As noted earlier, the strongly acidic pulping stage coupled with a subsequent hot alkaline extraction serves to remove the bulk of the lignin and hemicellulose fractions, resulting in a pulp with high alpha cellulose content. Since the conventional kraft process stabilizes residual hemicelluloses against further alkaline attack, it is not possible to obtain acceptable quality dissolving pulps through subsequent treatment in the bleach plant. In order to prepare dissolving type pulps by the kraft process, it is necessary to give the chips an acidic pretreatment before the alkaline pulping stage. A significant amount of material, on the order of 10% of the original wood substance, is solubilized in this acidic phase. Under the prehydrolysis conditions, the cellulose is largely resistant to attack, but the residual hemicelluloses have been degraded to a much shorter chain length (about 30% of the original DP) [27] and can therefore be removed to a large extent in the subsequent kraft cook by means of the well-known peeling reaction and other hemicellulose hydrolysis reactions. Primary delignification also occurs during the kraft cook. However, because of lignin condensation reactions during the acid stage, residual lignin in unbleached pulp from a

prehydrolyzed kraft process is more difficult to remove during bleaching compared to conventional kraft pulp.

The value of prehydrolysis is evidenced in a study on structural changes occurring in wood during this step. The prehydrolysis stage normally involves treatment of wood at elevated temperature (150-180°C) with dilute mineral acid (sulfuric or aqueous sulfur dioxide) or with water alone requiring times up to 2 h at the lower temperature [28]. In the latter case, liberated acetic acid from certain of the naturally occurring polysaccharides (predominantly the mannans in softwoods and the xylan in hardwoods) lowers the pH to a range of 3 to 4 [9]. This acidic treatment hydrolyzes a substantial portion of the hemicelluloses to short chain polymers and, to a lesser extent, to monomer form as a result of chemical treatment [30]. Whereas successive treatments of alkali and acid partially convert hemicelluloses to a resistant fraction remaining in the cell wall, the reverse sequence (acid-alkali) results in extensive hemicellulose fragmentation to readily solubilized components. Extensive studies on the chemistry and mechanism of prehydrolysis for both softwood [31a] and hardwood [32] have been carried out. The quantities and fates of the extracted constituents were determined as reaction conditions were varied. It is thus possible, depending on the severity of prehydrolysis, to produce pulps with varying alpha cellulose contents. A minimum level of purity must nevertheless be achieved for suitability in dissolving pulp applications.

Recently, the catalytic effect of anthraquinone in the alkaline phase of a prehydrolyzed soda dissolving pulp production has been presented [31b]. No adverse effects on end-use quality were noted for pulps prepared by the procedure.

3. Bleaching

Typical bleach sequences for dissolving pulps are shown in Table 62, and are discussed in detail in subsequent sections.

Following the bleaching, most pulp mills universally treat the bleached stock at 2.5-3.0 pH for approximately 5 min at low consistency to

Table 61A. Effect of combined SO₂ on acetate solution purity [25c].

	Cooking conditions					Acetylation test			
% Comb. SO₂	% Total SO₂	Max. temp.	Press. PSIG	Time Hours	Turb.	Col.	90° Scatter	Visc. *
1.15	5.5	147	85	8:15	12.4	24.1	118	84
0.65	7.0	130	95	10:15	8.0	15.1	60.6	100
0.4	15.0	127	150	5:50	6.0	12.8	31	100

* After constant acetylation time.